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A Study of Oxygen Functional Groups in Illinois Coal Fractions

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A Study of Oxygen Functional

Groups in Illinois Coal Fractions

(TITLE)

BY

Kenneth R. Osborne

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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1984

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A STUDY OF OXYGEN FUNCTIONAL

GROUPS IN ILLINOIS COAL FRACTIONS

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FOREWORD

"Contemporary coal technology is similar to the condition of oil refining technology prior to the introduction of high resolution mass spectrometry to decipher the nature of petroleum. Once a fundamental comprehension of the molecular nature of petroleums was at hand, industrial experts could optimize chemical and physical conditions for petroleum processing. The continuing excellence in refining technologies is founded on that initial investment."[1]

The above analogy of early petroleum history to the current challenge to establish a structure for coals, while encouraging and somewhat stirring to coal chemists, is not an exact one. Coals are more difficult to characterize due to their high molecular weight, low hydrogen content, high heteroatom content and their resulting insolubility. Consequently, results of coal structure research more often lead to to implications than to proofs. Conclusions drawn from this work will be offered with limitations or as confirmation or refutation of other work.

The difficulties of work of an analytical nature on a medium such as coal cannot be appreciated by the average chemist. One finds oneself "quantitatively" transferring a gooey black substance or vacuum filtering a water suspension that crawls up the side of the Buchner funnel.

It was at such times that I was reminded of the words of that renowned theoretical physicist, Ludwig Boltzmann: "Matters of elegance ought to be left to the tailor and the cobbler."[2] It is with that thought in mind that I offer this thesis to the scientific community.

ACKNOWLEDGEMENTS

I extend my appreciation to the faculty and staff of the Chemistry Department for their support and understanding during this work. I especially thank Dr's. Russ Carlson, Richard Keiter and Ed Sherman for their contribution of time and talent as members of my thesis committee. Dr. David Buchanan I sincerely thank for his patience and dedication in his attempt to make a stockroom supervisor "think like a chemist." He is responsible for any such behavior should it occur. I thank Linda Warfel for the ash determinations and Allan Wilcox for his help in preparing the C-22440 preasphaltene.

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ABSTRACT

Ferric chloride/acetic anhydride reacted with butyl phenyl ether in acetonitrile at 80° to give a 75.6% yield of p-butoxyacetophenone. Reactions with benzyl aryl ethers gave 30% cleavage. The reaction of benzyl phenyl ether gave 10.3% p-benzyloxyacetophenone as well as cleavage product. Reaction of a pyridine soluble, toluene insoluble fraction (preasphaltene) of an Illinois No. 6 coal with ferric chloride/acetic anhydride in acetonitrile gave a product 94% insoluble in pyridine. The insolubility was ascribed to condensation reactions.

Phenols were measured in coals, preasphaltenes and preasphaltene derivatives by acetylation with acetic anhydride in pyridine. Suggestions for improvement in the method were presented. Measurements over a period of time showed a decline in phenolic content in preasphaltenes that was attributed to air oxidation. No similar behavior was seen in the precursor coals. The insolubility of a preasphaltene of an Illinois No. 5 coal after drying was also evidence of air oxidation of that general fraction.

Reaction of preasphaltenes with pyridine hydriodide gave no significant decrease in molecular weights. The apparent molecular weight reductions observed by other workers were hypothesized to be the artifactual result of iodide salt incorporations.

INTRODUCTION

There is no doubt of the world's need to find a substitute for crude oil, whatever the controversy about the choice of substitute. Neither is there a doubt that known coal reserves are vastly greater than those of oil. The recent revival of interest in coal chemistry is due to that abundance.

Coal is no longer thought of as only a cheap fuel. It has become an organic resource that can be converted to liquid fuels suitable for movement by pipeline and to a variety of chemicals for commercial application.[3]

The three known processes for converting coal to liquid fuels were developed during the Second World War in Germany when that country faced a petroleum shortage.[4] The simplest method is to extend heavy fuel oil by dispensing in it finely ground coal as a colloid. This technique is limited in its use to boilers and blast furnaces.

The second method is by direct hydrogenation, under pressure, of powdered coal dispersed in a hydrocarbon solvent which increases the hydrogen to carbon ratio of the coal and thus produces liquid products. This method has been improved by the use of catalysts and there are several demonstration units (200 tons day^{-1}) using modifications of the original process. The primary products

must be treated further before they are useful as internal combustion fuels.

The requirements for petrochemical feedstocks are different than those for transport fuels. The basic building block of the present day petrochemical industry is ethylene. It is possible to make ethylene by steam cracking coal derived hydrocarbons. Coal derived feedstocks are much more aromatic than those that are petroleum based and are therefore much more resistent to cracking. It has been shown that if a mid-distillate fraction is hydrogenated before cracking, a much better yield of ethylene can be obtained. By this means, ethylene, propylene, C_4 hydrocarbons, benzene, toluene and xylenes, all of which are used in the petrochemical industry, can be produced.[5]

The third process for coal liquefaction is an indirect liquefaction based on the Fischer-Tropsch synthesis. The coal is initially heated with steam and air and the

$$C + O_2 + H_2 \xrightarrow{1500^{\circ}} CO + H_2 + CH_4$$

resulting gaseous mixture polymerized to liquid products. The problems of complete gasification are formidible and expensive.

The products of the above reaction, mainly a mixture of carbon monoxide and hydrogen known as synthesis gas, may be used without further preparation. As building blocks, these gases have more potential than ethylene. In

TABLE 1: Commercial CO Processes

$$Cl_2 + CO \xrightarrow[250^\circ]{\text{act.charcoal}} Cl\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl$$

$$C_6H_6 + HCl + CO \xrightarrow{AlCl_3} H\text{-}\overset{O}{\overset{\|}{C}}\text{-}C_6H_5$$

$$H_2 + CO \xrightarrow[250^\circ, 50 \text{ atm.}]{\text{Cu catalyst}} CH_3OH$$

$$CH_3OH + CO \xrightarrow[NaOH]{180^\circ, 15 \text{ atm}} H\text{-}\overset{O}{\overset{\|}{C}}\text{-}OCH_3$$

$$CH_3CH{=}CH_2 + H_2 + CO \xrightarrow[100^\circ, 15 \text{ atm.}]{\text{Rh catalyst}} CH_3CH_2CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}H$$

$$HC{\equiv}CH + CO \xrightarrow[H_2O]{Ni(CO)_4} H_2C{=}CH\text{-}\overset{O}{\overset{\|}{C}}\text{-}H$$

$$H_2C{=}CH_2 + CO \xrightarrow[H_2O]{Ni(CO)_4} H_3CCH_2\overset{O}{\overset{\|}{C}}\text{-}OH$$

$$CH_3OH + CO \xrightarrow[200^\circ, 15 \text{ atm.}]{I_2, \text{Rh catalyst}} CH_3\overset{O}{\overset{\|}{C}}OH$$

$$CH_3\overset{O}{\overset{\|}{C}}OCH_3 + CO \xrightarrow[\text{iodide catalyst}]{\text{metal catalyst}} CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3$$

TABLE 2: Potential Commercial CO Processes

$$CO + H_2 \xrightarrow[\text{and phosphine ligands}]{\text{Rh catalyst with nitrogen}} HO\text{-}CH_2CH_2\text{-}OH + CH_3\underset{OH}{C}HCH_2\text{-}OH$$

$$CO + H_2 \xrightarrow[190^\circ, 200 \text{ atm}]{\text{Co/Ni acetate catalyst}} CH_3CH_2\text{-}OH$$

$$C_6H_5\text{-}CH_3 \xrightarrow{CH_3CO_2H} C_6H_5\text{-}CH_2O_2CCH_3 \xrightarrow{CO} C_6H_5\text{-}CH_2CO_2H \xrightarrow{\text{reduction}} C_6H_5CH_2CH_2OH \xrightarrow{\text{dehydration}} C_6H_5CH{=}CH_2$$

$$C_6H_5\text{-}NO_2 \xrightarrow[190^\circ, 200 \text{ atm.}]{\text{noble metal catalyst}} C_6H_5\text{-}N{=}C{=}O$$

$$CH_3CO_2H + H_2 + CO \xrightarrow{Ru, I} CH_3CH_2CO_2H$$

$$H_2 + CO \xrightarrow[350^\circ, 10 \text{ atm.}]{\text{Ru/MnO catalyst}} CH_2{=}CH_2 + CH_3CH{=}CH_2 + \text{butylenes}$$

addition to the chemicals presently being produced from carbon monoxide (see Table 1), current research promises to create many more commercial processes (see Table 2).[6] Petroleum and natural gas will continue to be the dominant feedstocks for organic chemicals even after they become rare as fuels. Even so, chemicals based on synthesis gas should exhibit steady growth.

There are many problems as yet unsolved in coal utilization. Processes established on an experimental level will have to be established on scale sufficient to meet commercial needs. There is a dearth of engineers and technicians knowledgeable of coal plant operations. Enviornmental concerns for those living near coal processing plants need to be balanced against process economics.

The common thread running through the preceding presentation is the need for answers, improvements and modifications. The underlying need for more information about the structure of coal is pervasive. The information is needed, not only for the specific problems mentioned, but also for the classification of coals. The success of indirect hydrogenation, for example is especially dependent on the coal used.[7] Before major advances can be accomplished, better understanding of coal structure and of the variations of structure from one coal to another must be achieved.

Fundamental knowledge of coal structure is a relatively new pursuit. It has been stated[8] that coal science of today can be compared with the biochemistry of fifty to seventy-five years ago in the sense that the new tools required to answer fundamental questions were only then becoming available. Simple practial tests such as volatile matter yield, swelling and caking indices, ash yield, moisture content and light reflection were once the limit in the classification of coal. During the sixties and seventies, an outburst of instumental analysis was seen. Chromatographic separation techniques, infrared, NMR, mass spectrometry and combinations of these are now used on solid coal in major research laboratories.[3] Even with these advances, there is no modern accepted method of coal classification. Due to the highly complex structure of coal, information from these techniques often gives information of only a gross and sometimes speculative nature. It is in the pursuit of a finer definition of coal structure that traditional chemistry can play a role by focusing on target functional groups in coal and coal fractions. An as yet unrealized set of classification reactions, perhaps combined with spectral data, could be of great benefit to coal conversion technology. Qualitative definition of the environment of one functional group or a quantitative analysis procedure could have value in the determination of coal structure.

A great deal of effort has been expended on determining the role that oxygen plays in the structure of coal. Ultimate analysis of a typical Illinois Number 6 coal is shown in Table 3. Organic oxygen is usually calculated by subtracting from 100 the values for per cent carbon, hydrogen, nitrogen, sulfur and ash. This method has two disadvantages: 1) all the errors incurred in the other determinations are combined in the oxygen value; and 2) the ash does not represent the mineral matter as it was originally present in the coal.[9]

TABLE 3: Ultimate Analysis of a High Volatile Bituminous Illinois No. 6 Coal (PSOC 282)

	AS REC'D	DRY	DRY,ASH FREE
% ASH	9.37	10.15	
% CARBON	67.61	73.21	81.48
% HYDROGEN	4.73*	5.12	5.70
% NITROGEN	1.93	2.09	2.33
% SULFUR	1.25	1.35	1.50
% CHLORINE	0.21	0.22	0.25
% OXYGEN	7.24*	7.85	8.77

* Excludes Moisture

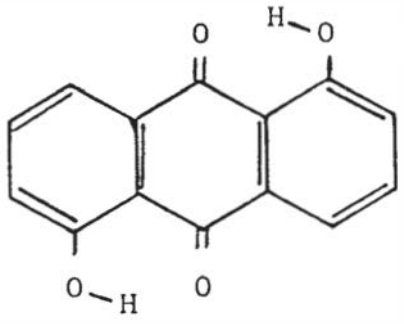
Phenolic groups account for 50-80% of the organic oxygen and represent virtually all the readily identifiable oxygen groups in bituminous coals. In low rank coals, carboxyl groups occur in appreciable amounts. These decrease with increasing rank (degree of coalification) and are not present in bituminous coals. The balance of oxygen present is believed to be present mainly as ether groups.[10] There is no direct method of measuring the organic oxygen without including in the

measurement the inorganic oxygen present.

Phenols in coal have been studied extensively because of their relatively high reactivity. Of the several methods[10] that have been used for measuring phenolic groups in coal, the acetylation method and silyl ether formation are the two generally accepted today. The acetylation method[11,12] consists of reaction of the coal or coal fraction with acetic anhydride in pyridine, generating the acetate of the phenol. The acetylated coal is then hydrolyzed and the resulting acetic acid distilled and titrated. The silation method[13] involves the reaction of coal with hexamethyldisilane to form trimethylsilyl ethers. Elemental analysis for silicon, as well as infrared and NMR have been used to quantitate the phenols present.

The acetylation method suffers by comparison with silation when derivitizing hindered or hydrogen bonded phenols. For example, compounds such as 1,5-dihydroxyanthraquinone (Figure 1) have been postulated to

FIGURE 1: Coal Model Representing Hydrogen Bonded Phenolic Groups



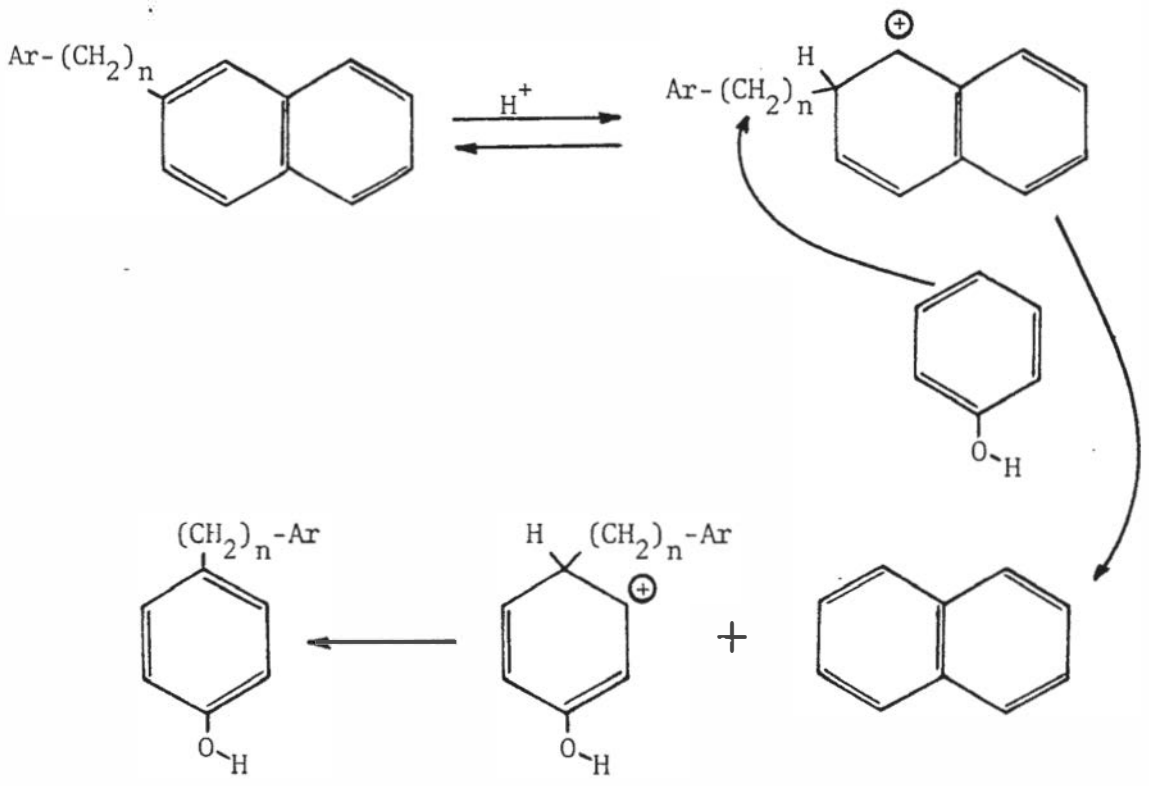
exist in coal. This compound forms trimethylsilyl ethers quantitatively on reaction with hexamethyldisilane at reflux. The highly hindered 2,6-di-tert-butylphenol reacts quantitatively with hexamethyldisilane in the presence of trimethylchlorosilane and pyridine to form the trimethylsilyl derivative.[14] These compounds are not acetylated with acetic anhydride/pyridine.

In addition to counting phenol groups, the work in this thesis includes further reactions of a derivitized phenol. The acetylation technique is the method of choice in this respect since the trimethylsilyl derivative is very subject to hydrolysis, generating the starting material. Difficult acetylations have been accomplished using aminopyridines as catalysts. The hindered phenolic group in 2,4,6-trimethyl-phenol is readily acetylated by acetic anhydride using p-dimethylamino-pyridine (DMAP) as catalyst.[15] This phenol is practically not acetylated by pyridine/acetic anhydride. Thus, the use of DMAP should assure the acetylation of sterically hindered phenols in coal. At the same time, a stable derivative of phenol would be available for further study.

Most coal chemists agree that coal is a cross-linked hydroaromatic macromolecular structure. These molecules are assumed to be composed of aromatic and hydroaromatic subunits linked together. Depolymerization of the molecules by the Heredy-Neuworth method[16] (Figure 2) is

thought to cleave the alkyl chains linking the subunits and gives products having number average molecular weights between 300 and 500. The nature of the crosslinks is a matter of some contention.

FIGURE 2: HEREDY-NEUWORTH DEPOLYMERIZATION METHOD



Mayo et. al.[17] used a variety of ether cleaving reagents to reduce the molecular weight of pyridine soluble, toluene insoluble fractions (preasphaltenes) of Illinois Number 6 coals. These reactions are summarized in Figure 3. There is accumulating evidence that ethers are an integral part of the coal matrix, crosslinking the coal subunits in some cases and thus contributing to the

FIGURE 3: Reactions Reducing the Molecular Weight of Preasphaltenes of Illinois No. 6 Coals

PREASPHALTENE* (M_n)		PRODUCT* (M_n, %I)
B35-A(1380)[18]	$\xrightarrow[5h,\ -35]{Na/NH_3/BuNH_2}$	C24-A(790,-)
U68-A(1283)[19]	$\xrightarrow[90°,\ 7d]{HI,\ H_2O}$	23-A(901,4.0%)
U68-A(1283)	$\xrightarrow[90°,\ 15d]{HI,\ C_6H_5CH_3}$	37-A(275,37.5%)
U68-A(1283)	$\xrightarrow[90°,\ 7d]{C_5H_5N,\ HI}$	V23-A(373,23.4%)
C1-D(1250)[20]	$\xrightarrow[42h,\ 50°]{(CH_3)_3SiI,\ CHCl_3}$	6-D(760,19%)**

* Sample numbers are Mayo's

** 6-D represents a fraction of the product

insolubility of coal.

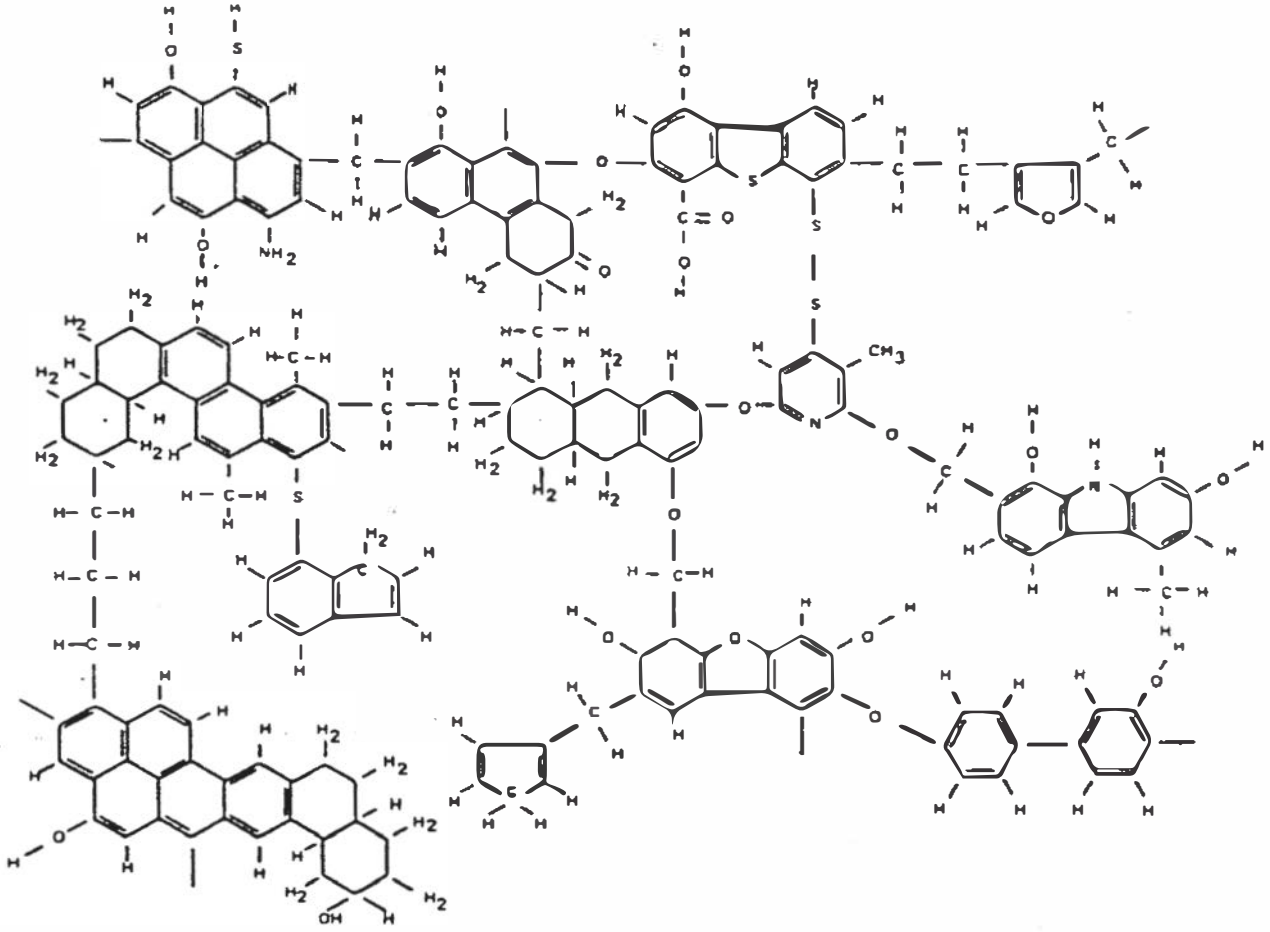
Part of the work in this thesis involved the reaction of ferric chloride and acetic anhydride with coal. These reagents had not previously been used in coal studies. The method was developed by Ganem et. al. as a means of removing aliphatic ether protecting groups.[21] Cleavage of chiral ethers gives evidence for a mechanism involving oxygen acylation followed by S_N1 or S_N2 attack by acetate. Cleavage of benzyl alkyl ethers gives evidence of two competing reactions: 1) cleavage of the ether, forming the corresponding acetates; and 2) acylation of the aromatic ring prior to ether cleavage providing only the alkyl acetate as an identifiable reaction product. Clearly, in proposing the use of this ether cleaving method on bituminous coal, where typically 65 percent of the carbons are aromatic carbons,[22] a more thorough investigation of reactions of aryl and benzyl ethers was in order. This thesis, in part, describes the cleavage of coal model ethers with ferric chloride/acetic anhydride as well as coal reactions with these reagents.

Those postulted ether cleaving reagents used by Mayo in Figure 3 include one reagent not generally known for ether cleavage, pyridine hydriodide. There is no evidence for cleavage of simple ethers by this reagent at the temperature cited.

The classical ether cleavage is the reaction of a hydrohalic acid such as hydrogen iodide with the ether in water. The mechanism for this reaction involves protonation of the ether oxygen, followed by S_N2 attack by the iodide ion. Such a protonation of the oxygen is impossible, however, in the presence of the more basic solvent, pyridine, used in Mayo's pyridinium iodide reaction. Yet he found evidence of ether cleavage not only by molecular weight reduction, but also by phenol group increase and by gel permeation chomatography studies. A possible explanation of this paradox is found in the recent paper of Larsen et.al.[23] This work shows that all hydroxyl groups in coal are within hydrogen bonding distance of a heteroatom that is not a hydroxyl hydrogen. The only element present in a quantity sufficient for this circumstance is oxygen and, as already stated, only ether oxygens are equivalent in number to hydroxyl oxygens.

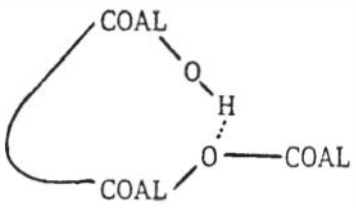
Larsen's work also emphasizes that coal is chemically complex. A model of coal by W.H. Wiser is shown in Figure 4.[24] The advantage of such models is that one can see the functional groups known or thought to be present. The disadvantages are that the functional groups are spread uniformly throughout the molecule seemingly at the whim of the creator (note the small c) and that the model represents a two dimensional structure. Given the fact that functional groups can be paired (either because the partners "found" each other sometime during the coalifi-

FIGURE 4: Coal Model



cation process or because the pairing results in a stable entity that survived that process) and the increased likelihood of such a pairing due to the coal molecule folding around itself and other such momecules, structures such as that in Figure 5 are possible. This struc-

FIGURE 5: Hydrogen Bonding of Phenols and Ethers in Coal



ture, were it present in coal, would explain Mayo's apparent ether cleavage with pyridine hydriodide. The ether oxygen is susceptible to attack by the iodide ion because it is, in effect, already protonated.[25]

If such structures exist in coal, it should be possible to cap the phenol group *via* acetylation with acetic anhydride/pyridine. This would result in the removal of the hydrogen bond from the ether and make it theoretically inert to the pyridine hydriodide. Reaction of two coal fractions, one with the phenolic groups intact, the other having been acetylated, should shed some light on the existence of the proposed structure in coal.

In summary, the purpose of this work is to:

1.) prepare a pyridine soluble, toluene insoluble fraction (preasphaltene) of an Illinois bituminous coal.

2.) count the phenolic groups in a preasphaltene by a.) acetylaton with acetic anhydride in pyridine using p-dimethylaminopyridine as a catalyst, b.)saponification of the acetates with base, c.) distillation of the acetic acid, and d.)titration.

3.)synthesize coal model ethers and apply the ether cleaving system of ferric chloride in acetic anhydride to those compounds.

4.) React the preasphaltene with ferric chloride/acetic anhydride and compare the molecular weight of the product with the preasphaltene.

5.) Isolate an acetylated preasphaltene.

6.) React the preasphaltene and the acetylated preasphaltene with pyridine hydriodide in pyridine and compare their respective molecular weights and phenolic group concentrations.

EXPERIMENTAL SECTION

General: Melting point determinations are uncorrected using a Thomas-Hoover capillary melting point apparatus. Nuclear magnetic resonance spectra were recorded on a Varian T-60 instrument; chemical shifts were measured relative to tetramethylsilane. Infrared spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer. Mass spectra were obtained using a DuPont 21-490 mass spectrometer. Elemental analyses are as received from Galbraith Laboratories, Knoxville, Tennessee.

Analytical thin layer chromatography was performed using 250 micron thick, precoated TLC plates with fluorescent indicator, distributed by Analtech Inc. GC analyses were carried out on a Varian Model 920 gas chromatograph utilizing a thermal conductivity detector. All GC columns were prepared by the author using copper tubing unless otherwise stated. Quantitative GC analyses were performed using a Sargent Model SR recorder with a disc integrator unless indicated otherwise.

HPLC analyses were accomplished on a Beckman Model 342 Gradient Liquid Chromatograph. All separations were effected with an Altex 4.6 mm. I.D. X 15 cm. Ultrasphere ODS column with 5 micron diameter particles. Eluted compounds were detected with a Beckman Model 160 Absobance Detector at a wavelenghth of 254 nanometers. The analytes

were recorded and quantitated on a Shimadzu Chromatopac C-RIB Data Processor.

Identification of compounds on GC and HPLC was performed in all cases by coinjection. Retention times are uncorrected.

Pyridine Hydriodide: To a magnetically stirred solution of 40 mL of dry pyridine (distilled from BaO) in 400 mL of toluene (dried over 4A molelular sieves) in a nitrogen atmosphere, was added HI gas (Union Carbide) at a flow rate of 8 mL min^{-1}. A 0.5 inch I.D. delivery tube was used to avoid stoppage by the precipitate. The HI addition was stopped after 1.25 hours as the stirring bar was ineffective due to the mass of off-white precipitate. Filtration and solvent removal in vacuo yielded 80.3 g (78.1%) of product. The solid was recrystallized from hot methanol to give near white crystals in an overall yield of 59.6%. The product was titrated with carbonate-free standardized NaOH and an average equivalent weight of 207.1 was obtained; the actual molecular weight is 207.102. The melting point (in a capillary sealed under vacuum) was found to be 278-280° . IR (cm^{-1}, KBr): 3210, 3050, 1650, 1510, 1470, 1320, 1055, 995, 745, 675. Anal. calcd. for C_5H_6NI: C,29.01; H,2.92; I,61.30. Found (Galbraith Laboratories, Knoxville, TN): C,28.89; H,2.92; I,61.52.

Phenethyl Tosylate: The tosylate was prepared in good yield using the method of Marvel and Sekera[26]. Phenethyl alcohol (Kodak, 32.4489 g, 0.266 mol) was reacted with 99.8 g (0.523 mol) of p-toluenesulfonyl chloride (Aldrich) in 500 mL of pyridine (Kodak) at 0^{o} for 15 hours. The entire contents of the reaction flask were poured into 2 L of ice and water. The resultant honey-orange oil crystallized with stirring. Filtration and drying (25^{o}, 2mm, 7h) yielded 70.9005 g (96.7%) of white crystals: mp 36.2-37.8^{o} (lit. =37.5-38.2^{o}); IR(cm^{-1},KBr) 2650, 1590, 1480, 1300, 1185, 1175; ^{1}HNMR(δ,CCl_4) 2.4(s,3H), 2.9(m,2H), 4.1(m,2H), 7.8(m,9H). The spectra are shown in Figures 7-9 on pages 57-59.

Phenyl Phenethyl Ether: The ether was prepared by the reaction of 40.9868 g (0.148 mol) of the impure tosylate, 15.2212 g (0.162 mol) of phenol (Mallinckrodt), 40 mL of a 25% aqueous solution of NaOH (0.032 mol) and 11.3302 g (0.0291 mol) of benzyltriphenylphosphonium chloride (Aldrich) at 85^{o} in 150 mL of chlorobenzene. After 18 hours of vigorous stirring, heat was removed and the reaction flask contents allowed to cool. The reaction mixture was added to 200 mL of water in a separatory funnel and the organic layer removed. The water layer was washed with chlorobenzene (3 X 50 mL) and the washes added to the original chlorobenzene solution; the solution was washed with water (3 X 100 mL), dried overnight

with anhydrous Na_2SO_4 and filtered. Solvent was removed in vacuo until a volume of 15-20 mL was attained.

A previous TLC study of the system had indicated that the product could be separated by a pseudo-chromatographic method. Dissolved, unreacted tosylate and catalyst were removed by addition of the 15-20 mL solution to a beaker containing 100 g of 60-200 mesh silica gel. Four 100 mL washes of petroleum ether (bp 35-60°) eluted the compound thought to be phenyl phenethyl ether from the silica gel. The petroleum ether was removed in vacuo to give 16.6965 g of residue. Gas chromatography (6% Analabs SE-30 on Varian Chromosorb W, 0.25 inch X 2m, 150° column temp.) showed the residue to be chlorobenzene (t_R= 0.56 min) and what was assumed to be phenyl phenethyl ether (t_R= 4.9 min). An NMR of the mixture was consistent with that assumption: (δ, CCl_4) 2.95(t,2H), 4.05(t,2H) 6.95(m,12.3H). The yield calculated from the NMR spectrum was 15.1 g (51.4%) of phenyl phenethyl ether.

A reaction similar to the former one was carried out using benzyltriethylammonium chloride as catalyst. Thirty mL of a 25% aqueous solution of NaOH (0.24 mol), 100 mL of chlorobenzene, 11.3100 g (0.120 mol) of phenol, 5.7078 g (0.020 mol) of catalyst and 29.8957 g (0.120 mol) of phenethyl tosylate were stirred vigorously for 18 hours at 85°. A work-up procedure identical with the former phenyl phenethyl ether synthesis gave product in an NMR

yield of 42.8%.

The two product ether solutions were combined and vacuum distilled to give 19.6961 g (38.7%) of colorless viscous liquid (110°, 2.4 mm): GC (6% SE-30 on Chromosorb W, $T_{col.}$= 150°) showed one peak, t_R= 4.9 min; ^{1}HNMR(δ,CCl_4) 2.95(t,2H), 4.05(t,2H), 6.95(m,10H); IR (cm^{-1},neat) 3060, 3040, 2870, 1590, 1380, 1240, 1170, 1045, 750, 688; mass spectrum: base peak m/e 105, parent peak m/e 198, p+1 peak height 4.8 (theoretically 4.31), p+2 peak height 0.4 (theoretically 0.346). The spectra are shown in Figures 9-12, pages 60-63.

Benzyl Phenyl Ether: To a flask containing 700mL of dichloromethane (Kodak) and 700 mL of water was added 55.8373 g (0.326 mol) of benzyl bromide (Aldrich), 30.7464 g (0.327 mol) of phenol (Mallinckrodt), 15.8068 g (0.395 mol) of sodium hydroxide (Fisher) and 22.2 g (0.0689 mol) of tetrabutylammonium bromide (Kodak). The flask contents were stirred vigorously for 22 hours at room temperature and the phases separated. The water layer was washed with diethyl ether (3 X 50 mL) and the washes added to the dichloromethane layer. The combined organic solution was washed with 5% NaOH (2 X 200 mL), 3 M HCl (100 mL) and $NaHCO_3$ (100 mL). The resulting cloudy solution became clear upon stirring with anhydrous Na_2SO_4 overnight. Vacuum filtration and solvent removal in vacuo gave wet crystals that were dried at room temperature and

1 mm Hg in an Abderhalden apparatus with a sulfuric acid trap. The dried crystals (mp 38.5-39.5°, lit.= 39°) weighed 61.0846 g (101.4%). An NMR spectrum of the crystals was consistent with benzyl phenyl ether with a trace of impurity at 1.0 δ. Recrystallization from hot ethanol gave 13.39 g of fluffy white crystals: mp 39.5-40.0°; ^{1}HNMR (δ,$CDCl_3$) 5.08(s,2H), 6.65-7.40(m,10H); IR (cm^{-1}, KBr) 3040, 1580, 1480, 1250, 1020, 745, 694. Spectra are shown in Figures 13-15, pages 64-66. Evaporation and refrigeration of the mother liquor gave 9.71 g (39.0-40.0°) and 20.87 g (38.5-40.0°) respectively of white crystals. Total recrystallized yield is 73.2%.

Benzyl Iodide: A solution of 100 g (0.67 mol of sodium iodide (Mallinckrodt) and 42.9631 g (0.251 mol) of benzyl bromide (Aldrich) in 500 mL of acetone was heated at reflux for 1.5 hours. The reaction solution was poured into 1.5 L of ice and water. The brown oil that formed crystallized upon scratching the side of the beaker. Suction filtration and air drying gave 47.5667 of yellow crystals. Recrystallization from hot ethanol and vacuum drying gave 11.3270 g (20.65%) of yellow needles, mp 21-22°(lit.= 24.5°). No further recrystallization was attempted due to the lachrymal effects of the product. GC (2 mm X 2 M glass column, 6% SE-30 on Chromosorb W, $T_{col.}$= 100°, flow = 60 mL/min) showed the product to be predominantly benzyl iodide (t_R= 3.0 min) with some benzyl

bromide (t_R= 1.8 min) present (integral ratio of 8:1). No attempt was made to further purify the iodide as the mixture served as well for a qualitative TLC and GC reference.

p-Benzyloxyacetophenone: To a solution of 0.4088 g 10.2 mmol) of sodium hydroxide in 50 mL of water was added 50 mL of dichloromethane, 1.7114 g (9.90 mmol) of benzyl bromide (Aldrich), 1.3830 g (9.95 mmol) of p-hydroxyacetophenone (Aldrich) and 1.6125 g (5.00 mmol) of tetrabutylammonium bromide (Kodak). The reaction mixture was stirred at room temperature for 27 hours. The reaction flask was placed in an ice bath and stirring continued. Hydrochloric acid was added until pH 2. The two phases were separated and the water layer extracted with diethyl ether (3 X 50 mL). The combined ether washes and dichloromethane layer were washed with 50 mL of 5% NaOH solution, 50 mL of water, stirred with anhydrous sodium sulfate and filtered. The solvents were removed in vacuo and the resulting off-white crystals dried in an Abderhalden drier with a sulfuric acid trap (25°,0.2 mm) to give 2.1352 g (95.3%) of product with a melting range of 90-92° (lit.= 93°). The product was recrystallized from hot ethanol to give 1.2796 g of white crystals: mp 91.5-92.5°; ^{1}HNMR(δ,$CDCl_3$) 7.90(d,2H), 7.35(s,5H), 6.95(d,2H), 5.10(s,2H), 2.50(s,3H); IR(cm^{-1},KBr) 1690, 1610, 1420, 1360, 1255, 1015; mass spectrum (m/e) 28, 39,

43, 51, 63, 65, 77, 91 (base peak), 92, 126 (parent peak). Spectra are shown in Figures 16-19, pages 67-70.

p-Butoxyacetophenone: To a solution of 4.5012 g (.112 mol) of sodium hydroxide in 250 mL of water was added 15.4695 g (.113 mol) of butyl bromide (Kodak), 15.5702 g (.114 mol) of p-hydroxyacetophenone (Aldrich), 17.1224 g (.0531 mol) of tetrabutylammonium bromide (Kodak) and 250 mL of chlorobenzene. The reaction mixture was heated at reflux and stirred vigorously for 19 h, at which time no change in the reaction mixture could be discerned with TLC. The reaction flask contents were cooled in an ice-salt bath. The phases were separated; the cold water layer was washed with 50 mL of chlorobenzene and the wash added to the original organic layer. The combined chlorobenzene portions were stirred in an ice bath with two 100 mL 1% sodium hydroxide washes and one 100 mL water wash. The solution was stirred overnight with anhydrous sodium sulfate, vacuum filtered and reduced in volume to approximately 40 mL. TLC using dichloromethane as eluent gave one spot (R_f=.50). Vacuum distillation of the yellow solution (203°,2.5 mm) gave 18.0660 g (83.3% yield) of a colorless, slightly viscous liquid: ^{1}HNMR(δ,$CDCl_3$) 7.90(d,2H), 6.90(d,2H), 3.95(t,2H), 2.45(s,3H),2.05-0.65(bm,7H);IR(cm^{-1}, neat)2970, 2940, 1660, 1590, 1430, 1255, 1175, 1070. Spectra are shown in Figures 20-22, pages 71-73.

p-Acetoxyacetophenone:[27] To a 100 mL flask containing 50 mL of CH_2Cl_2 was added 5.4942 g (39.5 mmol) of p-hydroxyacetophenone (Aldrich). Upon addition of 7.7 mL (95 mmol) of pyridine (MCB), the pale yellow solution turned light pink. Under a nitrogen atmosphere, a few drops of acetyl chloride (MCB) were added with an additon funnel to give a light mint green solution and a white precipitate. The precipitate slowly disappeared (3 min) and more acetyl chloride was added, regenerating the precipitate. This process was repeated until a precipitate formed that did not disappear. At that point, the solution turned a bright cloudy lemon yellow. The total amount of acetyl chloride added was 5.2 mL (73 mmol). The cloudy solution was heated at reflux for 30 minutes to give a clarified light golden orange solution. The solution was cooled, washed with 3 M HCl (3 X 50 mL), 5% $NaHCO_3$ (2 X 50 mL) and H_2O (2 X 50 mL) and stirred with anhydrous sodium sulfate overnight. Filtration and solvent removal *in vacuo* gave 6.7380 g of a dark brown gummy mass. TLC of the mass (50:50 CH_2Cl_2:hexane eluent) gave a spot at R_f=.10 and a spot that did not move.

The impure product was dissolved in 150 mL of 50:50 CH_2Cl_2:hexane solution and stirred with 22.4 g of 60-200 mesh silica gel. The solvent mixture was decanted and the silica gel washed (4 X 100 mL) with additional portions of the same solvent mixture until TLC gave no spot at R_f=.10. The washes were combined and suction filtered

through 10 g of silica gel. Solvents were removed *in vacuo* to give 5.5126 g of light yellow crystals. Recrystallization from hot ethanol gave 4.2027 g (59.6%) of white crystals: mp 52.5-53.5^{o} (lit.=54^{o}); ^{1}HNMR (δ,$CDCl_3$)8.00(d,2H), 7.20(d,2H), 2.55(s,3H), 2.88(s,3H); IR(cm^{-1}, KBr)3080, 3050, 2980, 1730, 1650, 1430, 1220. Spectra are shown in Figures 23-25, pages 74-76.

Acetylation of Phenol: A solution of 1.1009 g (11.7 mmol) of phenol (Mallinckrodt), 10.0 mL of acetic anhydride (MCB) and 20.0 mL of pyridine (Fisher) was heated at reflux for 12 hours. The honey-colored reaction mixture was added to 300 mL of water and extracted with four 75 mL portions of ether. The ether extractions were washed with 250 mL of 1 M HCl and 250 mL of water, dried with anhydrous sodium sulfate; solvent was removed in vacuo to a volume of 30 mL. Gas chromatography on a .25" X 19', 8% FFAP on chromosorb W column at a column temperature of 190^{o} and a flow rate of 100 mL min^{-1} showed solvent and phenyl acetate (t_R= 2.4 min) to be present. Using benzyl acetate as internal standard (t_R= 3.7 min), standard solutions were prepared and a working curve determined by the method of least squares (see Table 4, page 49). Because of the extreme sharpness of the two peaks their relative areas were determined by the peak height method. Calculations by this method gave a yield of 100%.

As a check of the peak height method under these conditions, two synthetic unknowns of phenyl acetate were prepared. These were determined gravimetrically to contain 1.2407 g and 1.0954 g. Standard solutions of phenyl acetate and benzyl acetate unique to this experiment were used to prepare a working curve. The "unknowns" were found to contain 1.22 g (98.3%) and 1.11 g (101.3%) of phenyl acetate.

The Conditions for Acetylation of Phenols Applied to Benzyl Phenyl Ether: To a solution of 20 mL of pyridine (distilled from BaO) and 10 mL of distilled acetic anhydride was added 1.4045 g (7.62 mmol) of the ether. The solution was heated at reflux for 24 hours. The dark brown reaction mixture was added to 200 mL of 1.5 M HCl and extracted with diethyl ether (4 X 50 mL). The ether extractions were washed with 5% NaOH (2 X 50 mL) and 50 mL of water, reduced to 10 mL in vacuo and vacuum distilled. The dark brown oil remaining in the distillation flask crystallized upon shaking. The crystals were dried for 5 hours (25°, 2 mm) in an Abderhalden apparatus to give 1.5977 g (114%) of brown crystals melting at $29-38^{\circ}$. The melting point of benzyl phenyl ether is 39°. Gas chromatography (.25" X 10' 11% dinonylphthalate on Chromosorb W column at a column temperature of 130° and flow rate of 60 mL min^{-1}) showed the presence of only benzyl phenyl ether and solvent. Thin layer chromatography of a

solution of the impure crystals using dichloromethane as eluent showed only benzyl phenyl ether (R_f= .81) and an unidentified material (R_f= 0-.20). A solution of p-benzyloxyacetophenone (0.425%) was prepared and a 0.5μL delivery of that solution on a TLC plate gave a dark, easily identifiable spot (R_f= .45). Proton NMR was consistent with benzyl phenyl ether as the only identifiable product in the reaction mixture: (δ,$CDCl_3$) 6.77-7.50(m,10H), 5.02(s,2H); extraneous small peaks were present at 2.14, 1.25 and 0.65-1.02. The product was recrystallized from hot ethanol and vacuum dried (2 mm) at room temperature to give 0.8377 g (59.0%) of off-white crystals: mp 39-40°; ^{1}HNMR(δ,$CDCl_3$) 6.75-7.62(m,10H), 5.08(s,2H). A mixed melting point with the starting ether was 39-40°.

The Conditions for Acetylation of Phenols Applied to Phenyl Phenethyl Ether: To a solution of 10 mL of distilled acetic anhydride and 20 mL of pyridine (distilled from BaO) was added 1.5738 g (7.88 mmol) of phenyl phenethyl ether. The reaction solution was heated at slow reflux for 23 hours. After cooling, addition of 200 mL of 1.5 M HCl caused the fine black suspension to become an opaque flocculent mass. A total of 500 mL of diethyl ether in 50 mL aliquots was used to extract the acidified reaction mixture. The ether extractions were reduced in volume in vacuo to 100 mL, washed with 5% $NaHCO_3$ (3 X 30

mL), 50 mL of water, dried with anhydrous $MgSO_4$ and vacuum filtered. The solution was further reduced in volume until a weight of 2.1321 g was attained. Injection on a .25" X 19', 8% FFAP on Chromosorb W column (T_{col} =210°, flow rate= 100 mL min^{-1}) showed only phenyl phenethyl ether (t_R= 7.9 min) and diethyl ether present. Quantitative GC (see Table 5) under the same conditions using diphenyl ether as internal standard (t_R= 3.4 min) gave a 99.5% recovery of the starting ether.

Determinative Reaction of Benzyl Phenyl Ether with Ferric Chloride/Acetic Anhydride (3h,25°): To a flask containing 1.2434 g (6.74 mmol) of benzyl phenyl ether and 0.50 g (6.2 mmol) of anhydrous ferric chloride (Alfa) was added 10 mL of acetic anhydride. The reaction mixture was stirred at room temperature for three hours. The reaction flask contents were vacuum filtered with number three Whatman paper, added to 20 mL of 2 M sulfuric acid and stirred. The pH was adjusted to 8 with a saturated sodium bicarbonate solution. The neutralized reaction mixture was extracted with three 30 mL portions of diethyl ether. Biphenyl (0.6407 g) was added to the ether extractions as internal standard and the solution dried by stirring overnight with anhydrous sodium sulfate. Quantitative gas chromatography (0.2 mm X 2M glass column, 6% SE-30 on Chromosorb W, $T_{col.}$=95°, He=60 mL min^{-1}) as shown in Table 6 gave yields of 6.1% for

phenyl acetate (t_R=1.2 min) and 8.4% for benzyl acetate (T_R=2.1 min); t_R for bibenzyl = 6.4 min.

Qualitative gas chromatography using the above column at 175° and a flow rate of 80 mL min^{-1} gave peaks not accounted for at retention times of 3.6 and 5.1 minutes. Benzyl phenyl ether (t_R= 1.7 min) and p-benzyloxyacetophenone (t_R=1.5 min) were not present.

Determinative Reaction of Benzyl Phenyl Ether with Ferric Chloride/Acetic Anhydride (3h,77°): To a flask containing 0.50 g (3.1 mmol) of ferric chloride (Alfa) and 1.9173 g (10.41 mmol) of benzyl phenyl ether was added 12 mL of acetic anhydride. The reaction mixture was heated at an oil bath temperature of 77° for three hours. The reaction mixture was cooled in an ice bath prior to the slow addition of 30 mL of 2 M sulfuric acid. The pH was adjusted to 8 with sodium bicarbonate. The neutralized reaction mixture was extracted with three 30 mL portions of diethyl ether. The combined ether extractions were washed with three 30 mL portions of a saturated sodium chloride solution. The ether solution was added to a flask containing 0.9861 g of biphenyl. After drying with anhydrous sodium sulfate, gas chromatography (0.25" X 6' 6% SE-30 on Chromosorb W, $T_{col.}$=110°, He=85 mL min^{-1}) gave yields of 29.4% and 22.6% for phenyl acetate (t_R=1.4 min) and benzyl acetate (t_R=2.2 min) respectively. See Table 7 for GC analysis.

Qualitative gas chromatography ($T_{col.}$=170°) gave peaks not accounted for at retention times of 3.2 and 4.5 minutes. Benzyl phenyl ether (t_R=1.9 min) was not present.

Determinative Reaction of Benzyl Phenyl Ether with Ferric Chloride/Acetic Anhydride (24h, 80°): To a flask containing 1.8343 g (9.96 mmol) of benzyl phenyl ether and 0.50 g (3.1 mmol) of ferric chloride (Alfa) was added 10 mL of acetic anhydride. The reaction mixture was heated at an oil bath temperature of 80° for 24 hours and cooled in an ice bath prior to the addition of 30 mL of 2 M sulfuric acid. The pH was adjusted to 8 with sodium bicarbonate and a saturated sodium bicarbonate solution and the neutralized reaction mixture extracted with three 30 mL portions of diethyl ether. Biphenyl (0.9519 g) was added as internal standard and the solution dried overnight with anhydrous sodium sulfate. Gas chromatography (0.25" X 6' 6% SE-30 on Chromosorb W, $T_{col.}$=110°, He=85 mL min^{-1}) gave yields of 44.0% for phenyl acetate (t_R=1.4 min) and 27.8% for benzyl acetate (t_R=2.2 min).

Qualitative gas chromatography ($T_{col.}$=170°) gave peaks not accounted for at 3.2 and 4.5 minutes. Benzyl phenyl ether (t_R= 1.9 min) was not present. See GC data, Table 7.

Reaction of Phenol with Ferric Chloride/ Acetic Anhydride: Phenol (3.0943 g, 32.88 mmoL), 1.0 g of ferric

chloride (6.16 mmoL) and 15 mL of acetic anhydride were heated at 97° for 23 hours. The cooled reaction mixture was extracted with ether to give 38.3027 g of solution. Benzyl acetate (1.1198 g) was diluted with 5.2458 g of the extract. Standard solutions of phenyl acetate and benzyl acetate were prepared (see Table 8). GC analysis (6% SE-30 on Chromosorb W, $T_{col.}$=150°) gave a 100% yield for phenyl acetate.

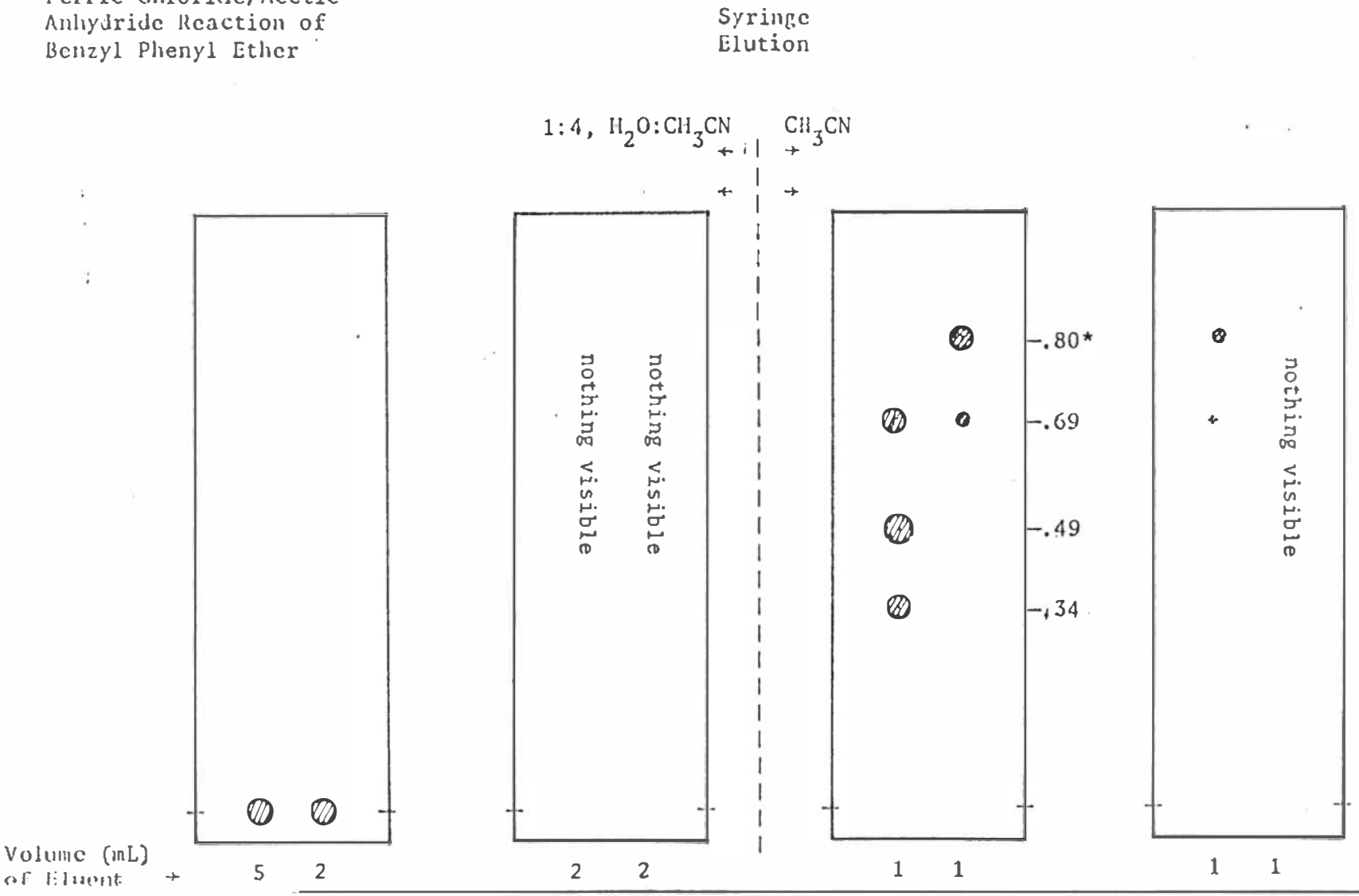
Preparation of Ferric Chloride/Acetic Anhydride Reaction Mixtures for HPLC Study: This method was initially developed during a cleavage reaction of benzyl phenyl ether but all subsequent HPLC determinations of ether reactions with ferric chloride and acetic anhydride in acetonitrile were carried out using the same preparative technique. A trial and error approach was used to determine solvent mixtures for the separation. A C_{18} Sep-Pak^R cartridge (containing the same reverse phase material as the HPLC column) was used to selectively retard the compounds in the supernant of a centrifuged reaction mixture. The Sep-Pak^R was fitted with a 5 mL syringe and wetted with acetonitrile. Two mL of water were placed in the syringe, followed by one mL of the supernant (which included an appropriate amount of internal standard in the case of quantitative determinations) and two additional mL of water. The syringe plunger was placed in the barrel only to the extent of preventing

escape of material during shaking. After thorough mixing, the syringe contents were forced through the Sep-Pak^{R}. Three 2 mL portions of an 80:20 water:acetonitrile solution were forced through the cartridge and collected individually. A series of 1 mL acetonitrile elutions of the cartridge were collected. The eluent components were resolved by TLC (see Fig. 6). HPLC analysis was possible by selection and combination of those eluents containing organic compounds.

Reaction of Ferric Chloride/Acetic Anhydride with Benzyl Phenyl Ether: To a 50 mL flask was added 1.0423 g (5.657 mmol) of benzyl phenyl ether, 1.6 mL (17 mmol) of acetic anhydride, 1.1849 g (7.305 mmol) of ferric chloride and 15 mL of acetonitrile (Baker HPLC grade). The flask was fitted with a condenser and the contents heated at reflux for 3.5 h in a nitrogen atmosphere. The reaction mixture was cooled in an ice bath and centrifuged (Clay-Adams Analytical). The supernant and acetonitrile rinses were diluted with acetonitrile to 25 mL in a volumetric flask (solution 21-1). Chlorobenzene (0.1244 g) was weighed into a 25 mL volumetric flask and diluted to the mark with solution 21-1. The contents of the flask were mixed and immediately subjected to the previously described Sep-Pak^{R} separation method.

HPLC (mobile phase of 80% CH_3CN/20% H_2O, flow = 0.8 mL min^{-1}) of the collected organic fractions (solution 21-4)

FIGURE 6: TLC's of Eluents From Sep-Pak Separation of Ferric Chloride/Acetic Anhydride Reaction of Benzyl Phenyl Ether



gave evidence for the presence of phenyl acetate (t_R=2.95 min), benzyl phenyl ether (t_R=5.07 min), p-benzyloxyacetophenone (t_R=3.88 min) and p-acetoxyacetophenone (t_R=2.75 min). Peaks of undetermined origin were found at retention times of 2.34, 2.67, 2.84, 4.67, 6.37, 8.99 and 10.09 minutes. Benzyl acetate was found not to be present. Chlorobenzene (internal standard) gave a retention time of 4.32 min.

Calibration standards were prepared containing phenyl acetate, benzyl phenyl ether and chlorobenzene and a working curve determined on HPLC (see Table 10). Solution 21-4 was used to determine the yield of phenyl acetate (30.0%) and the recovery of benzyl phenyl ether (1.65%).

Calibration standards were prepared containing p-acetoxyacetophenone and chlorobenzene (see Table 10) and a working curve determined on HPLC. Solution 21-4 was used to determine the yield of p-acetoxyacetophenone to be 0.00587%.

Standard solutions containing p-benzyloxyacetophenone and biphenyl (internal standard, t_R=5.65 min) were prepared (see Table 10) and a working curve determined on HPLC. Biphenyl (0.0081 g) was diluted in a 10 mL volumetric flask with solution 21-1 and the resulting solution immediately subjected to the Sep-Pak^R treatment. HPLC analysis gave a 10.3% yield of p-benzyloxyacetophenone.

Reaction of Ferric Chloride/ Acetic Anhydride with Butyl Phenyl Ether: (During the first of the following two analyses, p-butoxyacetophenone was not available in pure form. The second reaction was run to determine the amount of that substance.) Reaction 1: To a flask containing 0.8354 g (5.561 mmol) of butyl phenyl ether (Aldrich) and 1.6 mL (17 mmol) of acetic anhydride was added 1.1636 g (7.174 mmol) of ferric chloride and 15 mL of acetonitrile (Baker HPLC grade). The reaction mixture was heated at reflux for 3.5 h under nitrogen, cooled in an ice bath and centrifuged (Clay-Adams Analytical). The supernant and acetonitrile washes were diluted to 25 mL in a volumetric flask with acetonitrile (solution 36-1). One mL of the solution was subjected to the Sep-Pak^{R} treatment. HPLC (80% CH_3CN,20% H_2O at 0.8 mL min^{-1}) gave evidence for butyl phenyl ether (t_R=6.46 min) and p-butoxyacetophenone (t_R=3.16 min). Phenyl acetate was not present. Peaks of unknown origin were present at retention times (flow rate = 0.6 mL min^{-1}) of 7.70, 8.60, 9.24, 10.19, 14.09, 16.72, 18.42 and 20.95 minutes.

Standard solutions were prepared containing butyl phenyl ether and bibenzyl (t_R= 7.53 min @ 0.8 mL min^{-1}) and a working curve determined on HPLC (see Table 11). A solution of 0.0382 g of bibenzyl diluted to 10 mL in a volumetric flask with solution 36-1 was prepared. Sep-Pak^{R} treatment and analysis by HPLC gave a recovery of 7.64% for butyl phenyl ether.

Reaction 2: To a flask containing 0.8243 g (5.49 mmol) of butyl phenyl ether (Aldrich) and 1.6 mL (17 mmol) of acetic anhydride was added 1.1117 g (7.40 mmol) of ferric chloride and 15 mL of acetonitrile (Baker HPLC grade). The reaction mixture was heated at reflux for 3.5 h under nitrogen, cooled in an ice bath and centrifuged (Clay-Adams Analytical). The supernant and acetonitrile washes were diluted to 50 mL in a volumetric flask (solution 53-3).

Standard solutions were prepared containing p-butoxyacetophenone (t_R= 3.30 min) and acetophenone (t_R= 2.84 min) and a working curve (see Table 11) determined on HPLC (80% acetonitrile, 20% water at 0.8 mL min^{-1}). A solution of 0.1268 g of acetophenone diluted to 10 mL in a volumetric fask with solution 53-5 was prepared. Sep-Pak^R treatment and analysis by HPLC gave a 75.6% yield of p-butoxyacetophenone.

Reaction of Ferric Chloride/ Acetic Anhydride with 2-Naphthyl Benzyl Ether: To a flask containing 1.2587 g (5.34 mmol) of 2-naphthyl benzyl ether[28] and 1.5 mL (16 mmol) of acetic anhydride was added 1.1403 g (7.59 mmol) of ferric chloride and 20 mL of acetonitrile (Baker HPLC grade). The mixture was heated at reflux for 3.5 h under nitrogen. The contents of the reaction flask were cooled and centrifuged (Clay-Adams Analytical). The supernant and acetonitrile washes were diluted with acetonitrile to

50 mL in a volumetric flask (solution 43-1). One mL of the solution was subjected to the Sep-Pak^R treatment. HPLC (80% acetonitrile, 20% water at 0.6 mL min^{-1}) showed the presence of 2-naphthyl acetate (t_R= 4.58 min) and 2-naphthyl benzyl ether (t_R= 11.08 min) and the absence of benzyl acetate.

Standard solutions of 2-naphthyl acetate (Aldrich), 2-naphthyl benzyl ether and naphthalene (internal standard, t_R= 6.36 min) were prepared and a working curve determined (see Table 12) on HPLC. Solution 43-1 was used to dilute 0.0575 g of naphthalene to 10 mL in a volumetric flask. One mL of that solution was subjected to the Sep-Pak^R treatment and injected on HPLC to give a 29.5% yield of 2-naphthyl acetate and a 12.1% recovery of 2-naphthyl benzyl ether.

Preparation of Pre-asphaltene 252: A 178.4 g sample of Illinois No. 5 coal (Penn State Data Bank PSOC 252) was placed in a ball mill jar previously flushed with nitrogen. Sixteen grinding cylinders (Sargent-Welch) were added and the jar rotated for one hour on a ball mill. The ground coal was sieved using a shaker (Pulverit Type 3020 at a setting of 6) to give 77.2 g of smaller than 120 mesh coal. The ball mill jar was flushed with nitrogen, 11 additional cylinders added and the coal not passing the 120 mesh sieve reground and resieved to give a total of 171.0 g of smaller than 120 mesh coal.

A portion (60.1 g) of the ground coal was extracted for 3 h with 1.5 L of pyridine (distilled from BaO) at reflux. The extraction mixture was allowed to cool and suction filtered using no. 1 Whatman filter paper to give an opaque black solution. Successive extractions were carried out until the fourth extraction gave a solution the color of weak tea. The remainder of the 171.0 g sample was treated similarly. Pyridine was removed from the filtrates on a rotary evaporator until 100 mL of black slurry remained. The slurry was poured into 1.2 L of toluene, stirred for 1 h and vacuum filtered. The black gummy residue in the Buchner funnel was washed with 10% HCl (4 X 50 mL) and water (5 X 50 mL).The pre-asphaltene fraction was dried in an Abderhalden apparatus (100°, 0.2 mm) until a three hour drying time gave only a 0.1% change in weight. The total pyridine soluble, toluene insoluble fraction weighed 18.0052 g (10.5%): 1.22% ash, 4.28 mmol phenol g^{-1}.

The extracted coal (pyridine insoluble) resulting from a series of extractions of one portion (85.2 g) of whole ground coal was added to 2 L of 10% HCl, stirred for 5 h, suction filtered, rinsed with water (3 X 250 mL),stirred with 250 mL of water for 2 h, refiltered and dried in an Abderhalden apparatus (100°,0.2 mm) to give 74.444 g of dried extracted coal. Pyridine used for extractions was dried over KOH and distilled from BaO for further extrac-

tion use.

Elemental analysis and molecular weight determination of the pre-asphaltene were performed by Galbraith Laboratories (Knoxville, TN): 72.77% C, 5.22% H, 2.78% N; the sample was reported not to be entirely soluble in pyridine.

A 14.092 g sample of pre-asphaltene 252 was placed in a 3 L flask with 1.5 L of pyridine, stirred under nitrogen at room temperature for 24 h and filtered in a ASTM 25-50 μ fritted funnel. Solvent was removed in vacuo. Two additional cycles of extraction, filtration and solvent removal were performed giving a total of 50 mL of black slurry.

That coal from the above 14.0920 g sample not soluble in pyridine was vacuum filtered and air dried for 10 minutes. The yield of non-dry, extracted coal was 1.6137 g.

The slurry from the pyridine soluble fraction of the 14.092 g sample was poured into a flask containing 800 mL of toluene, stirred under nitrogen 3 days and vacuum filtered. The filter funnel contents were stirred under nitrogen with 800 mL of 5% HCl overnight. Filtration and drying (100°,.05 mm) of the precipitate yielded 12.7470 g. This product proved not to be entirely soluble in pyridine. Further attempts to obtain a pyridine soluble fraction did not meet with success.

Preparation of Pre-asphaltene 282: A 150.7 g sample of Illinois No. 6 coal (Penn State Coal Data Bank PSOC 282) was placed in a ball mill jar, previously flushed with nitrogen, containing sixteen grinding cylinders (Sargent-Welch). The jar was rotated on a ball mill for 3 h. The coal was sieved (ASTM 120 and 200 mesh) in a nitrogen atmosphere using a shaker (Pulverit Type 3020 at a setting of 6) to produce 137.0 g passing the 200 mesh screen and 3.0 g passing the 120 mesh screen but not the 200.

A 31.6 g sample of the smaller than 200 mesh coal was extracted with 250 mL of pyridine (distilled from BaO) under nitrogen for 12 h. The mixture was centrifuged (Sorvall Superspeed) and the supernant gravity filtered (Whatman No. 1) under nitrogen. The black, opaque filtrate was stripped of pyridine until a black slurry was obtained. The slurry was allowed to cool while still under reduced pressure and the rotary evaporator flushed with nitrogen. The slurry was added to a volume of toluene 10 times that of the slurry (typically 200 mL of toluene). The extracted coal was added to a fresh 250 mL of pyridine and the process repeated until the fifth extraction filtrate was a clear tea colored solution. A 47.5 g portion of smaller than 200 mesh coal was subjected to the same treatment. Pyridine from the stripping of the filtrates was dried over KOH for 2 days and distilled from BaO for further extractions.

The toluene mixtures were kept under nitrogen in a

common flask until the extractions were complete. The precipitated coal fraction was gravity filtered, stirred for 2 days in 1600 mL of 5% HCl, gravity filtered and rinsed with water; all processes were accomplished in a glove bag under nitrogen. The pre-asphaltene was dried to constant weight in an Abderhalden apparatus (100°, 0.2 mm) to give 7.8331 g (9.9% yield from coal) of product: 76.38% C, 5.37% H, 2.49% N, 1.03% S; M_n= 1247, 1.25% ash, 4.78 mmol phenol g^{-1}.

Pre-asphaltene C-22440: A 143 g sample of an Illinois No. 6 coal (Illinois Geological Survey #C-22440) was added to 600 mL of pyridine in a one L flask. The flask was placed in an ultrasonic cleaner (Bransonic, 50 watts) for 15 minutes under nitrogen. The pyridine suspension was centrifuged (9000 rpm, Sorvall SS-1). The supernant was vacuum filtered (Whatman #1), deoxygenated by bubbling N_2, distilled to a slurry under water aspirator vacuum and allowed to cool before the vacuum was broken with nitrogen. The sediment from the centrifuge tube was returned to the liter flask with 600 mL of fresh pyridine. The process of ultrasonic extraction, centrifugiation, filtration and distillation was repeated five times. The combined distillation bottoms (150 mL) were poured into 1.5 L of toluene, stirred for 10 hours and vacuum filtered (Whatman #1). The toluene insoluble fraction was stirred overnight with 1 L of 10% HCl, vacuum

filtered, washed with water (3 X 150 mL) and dried in an Abderhalden apparatus (100°,0.2 mm) to give 16.5519 g (11.5%) of product (99-1): 78.23% C, 5.50% H, 2.23% N, 1.08% S; 0.88% ash; 4.44 mmol phenol g^{-1}; M_n = 1322.

Ash Determination Procedure: Ash determinations of coals and pre-asphaltenes were performed in accordance with standard procedure ASTM 3174 . A crucible was cleaned by gently heating a solution of 0.5 mL of concentrated HCl and 3 mL of concentrated HNO_3 therein until reddish brown fumes of NO_2 were evolved. The crucible was allowed to cool and rinsed with water. The crucible was dried to constant weight over a Meeker burner (3h), cooled for 2 minutes on a flat porcelain plate and transferred to a desiccator for further cooling and weighing.

A sample of the coal or coal fraction (100-150 mg) was weighed into the dried crucible. The crucible was placed in a cold muffle furnace. Heating was initiated at a thermostat setting of 30 so that a temperature of 500° was achieved in 1 hour and a temperature of 750° in 2 hours. After 2 hours, the thermostat setting was changed to 25 to maintain the furnace temperature at 750° and the coal heated one additional hour. The crucible was removed, cooled on a porcelain plate for 2 minutes, placed in a desiccator for further cooling and weighed.

Determination of Phenolic Groups in Coal and Coal Fractions: The method of van Krevelen et. al.[11] for the determination of phenols in coal was modified by the employment of p-dimethylaminopyridine in addition to reagents used in that work. The coal or coal fraction (0.5000-1.0000 g) was added to a solution of approximately 0.15 g of p-dimethylaminopyridine (Aldrich) in 10 mL of pyridine (distilled from BaO). Five mL of distilled acetic anhydride were added. The reaction mixture was heated at reflux for 24 h under nitrogen, cooled, added to 100 mL of water, suction filtered and washed with water (5 X 30 mL). The filtration residue was transferred to a 100 mL flask; 2 g of $Ba(OH)_2$ and 50 mL of water were added. The mixture was heated at reflux under nitrogen for 5 h, cooled, 2 mL of conc. H_3PO_4 added and 40 mL of the flask contents distilled and collected. The distillate was titrated with 0.02785 M carbonate-free NaOH using 0.03694 M HCl for back titrations and phenolphthalein as indicator. Water (40 mL) was added to the distillation flask. The process of distillation and titration was continued until there was little change in the volume of titrant used (typically 15 cycles).

Reaction of Pre-asphaltene 282 with Ferric Chloride/ Acetic Anhydride: A solution of 2.7281 g of ferric chloride in 50 mL of acetonitrile was centrifuged (Sorvall Superspeed) and the supernant added to a flask

containing 0.9451 g of pre-asphaltene 282 and 3 mL of distilled acetic anhydride. The reaction mixture was heated at reflux under nitrogen for 6 days and cooled. Acetonitrile was added to give a total volume of 75 mL, the mixture stirred overnight under nitrogen and centrifuged (Sorvall Superspeed). Further acetonitrile extractions (3 X 75 mL) and centrifugations were performed. The combined supernants were filtered (No. 1 Whatman) and solvent removed in vacuo to give approximately 15 mL of solution; the solution was added to 150 mL of 10% HCl and stirred under nitrogen overnight. The precipitated fraction was centrifuged and washed with 10% HCl (3 X 100 mL) until a test of the wash for ferric ion with Ferron (8-hydroxy-7-iodo-5-quinolinesulfonic acid)[29] proved negative; an additional 100 mL water wash was performed. The fraction was dried to constant weight in an Abderhalden dryer (100°,0.2 mm) to give 0.0558 g of brown product (65-1SA2).

The fraction of product insoluble in acetonitrile was washed with 10% HCl (2 X 100 mL) until the ferric ion test proved negative and with 100 mL of water. Drying at 100° and 0.2 mm gave 0.7414 g of black pre-asphaltene like product (65-1UA): 1.44% ash, 69.62% C, 4.93% H, 1.94% N.

Solubility tests of sample 65-1UA were performed in pyridine, chloroform and toluene. The respective 0.1713 g, 0.1962 g and 0.1891 g samples were stirred with 250 mL

of the solvent. The product was judged to be insoluble in all the solvents due to lack of coloration of the solvent. No quantitative recovery of the insoluble products was attempted.

A simultaneous blank reaction was run under identical conditions using 0.9093 g of pre-asphaltene 282, 3 mL of acetic anhydride and 50 mL of acetonitrile. The reaction product was extracted with acetonitrile in a manner identical with the above experiment to give 0.1594 g soluble dried product and 0.6534 g of insoluble dried product. Solubility tests of the acetonitrile insoluble fraction (65-2UA) were performed. A 0.1713 g sample was entirely soluble in 250 mL of pyridine as evidenced by lack of precipitate on centrifugation; the dry recovered sample weighed 0.1394 g (84%). The 65-2UA sample (0.1943 g) failed to color toluene and 69% was recovered. Chloroform extraction (250 mL) of a 0.1898 g portion of 65-2UA produced an orange-brown solution and a precipitate. The dried chloroform insoluble portion weighed 0.1316 g and the soluble portion weighed 0.0165 g (78% recovery).

Saponification of Fraction 65-1UA: To a 0.1665 g sample of fraction 65-1UA was added 2.1g of $Ba(OH)_2$ and 40 mL of water. The reaction mixture was heated at 100° under nitrogen for 6 hours and left in the cooling oil bath overnight. To the cooled reaction mixture was added 6 M HCl until the supernant was acidic to Congo Red.

Sodium hydroxide (5%) was added until the mixture was just basic to litmus. The mixture was stirred for 3 hours, suction filtered, washed with water (2 X 100 mL), 10% HCl (3 X 250 mL), water (3 X 100 mL) and dried in an Abderhalden apparatus (100°, 0.2 mm) to constant weight (0.1204 g). The product was insoluble in pyridine.

Reaction of Preasphaltene 282 with Pyridine Hydriodide: Preasphaltene 282 (0.2178 g), pyridine hydriodide (0.1489 g) and 15 mL of pyridine (distilled from BaO) were heated (oil bath = 54°) and stirred under nitrogen for 6 days. The reaction mixture was cooled, added to 400 mL of 10% HCl, stirred overnight and vacuum filtered. The precipitate was washed with water (3 X 100 mL) and dried to constant weight in an Abderhalden apparatus (100°, 0.2 mm) to give 0.1607 g of product (93-1): 76.14% C, 4.96% H, 2.24% N, 2.01% I; 7.2 mmol phenol g^{-1}; M_n = 1119.

Acetylation of Preasphaltene 282: The preasphaltene was acetylated by a modification of the method of van Krevelan et al.[11] The preasphaltene (0.7572 g) was added to a solution of 0.1321 g of p-dimethylaminopyridine (Aldrich) in 17 mL of pyridine (distilled from BaO) and 8.5 mL of distilled acetic anhydride. The reaction mixture was heated at reflux under nitrogen for 24 hours, cooled and the volume reduced *in vacuo* by half. The

mixture was cooled under vacuum, added to 200 mL of 5% HCl, stirred for 24 hours under nitrogen and centrifuged. The precipitate was stirred with 200 mL of water, suction filtered, washed with water (2 X 100 mL) and transferred to an Abderhalden drying apparatus (100°, 0.2 mm). The dry product (79-1) weighed 1.0216 g (135%): 72.99% C, 4.83% H, 2.36% N, 0.54% S.

Reaction of Acetylated Preasphaltene 282 with Pyridine Hydriodide: The acetylated preasphaltene (0.4205 g), pyridine hydriodide (0.2252 g) and 20 mL of pyridine (distilled from BaO) were heated (56°) in an oil bath for 8 days under nitrogen. The reaction mixture was cooled, added to 400 mL of 10% HCl, stirred overnight and vacuum filtered. The precipitate was washed with water (3 X 150 mL) and dried to constant weight in an Aberderhalden apparatus (100°, 0.2 mm) to give 0.3482 g (82.8%) of product (103-1): 73.75% C, 4.98% H, 2.55% N, 1.77% I; 5.88 mmol phenol g^{-1}.

Reaction of Preasphaltene C-22440 with Pyridine Hydriodide: The preasphaltene (0.9400 g), pyridine hydriodide (0.6276 g) and 60 mL of pyridine (distilled from BaO) were heated (oil bath = 54°) and stirred under nitrogen for 6 days. The reaction mixture was cooled, added to 600 mL of 3 M HCl, stirred overnight and vacuum filtered. The precipitate was washed with water (4 X 150 mL) and dried to a constant weight in an Abderhalden

apparatus (100°,0.2 mm) to give 0.9628 g (102 %) of product (108): 72.54% C, 5.26% H, 2.03%N, 6.06%I; 7.06 mmol phenol g^{-1}; M_n=1222.

Acetylation of Preasphaltene C-22440: The preashaltene (1.5162 g) was added to a solution of 0.1565 g of p-dimethylaminopyridine (Aldrich) in 20 mL of pyridine (distilled from BaO) and 10 mL of distilled acetic anhydride. The reaction mixture was heated at 100° under nitrogen for 5 days, cooled, stirred with 250 mL of 3M HCl and vacuum filtered. The precipitate was washed with water (3 X 200 mL) and transferred to an Abderhalden apparatus (100°, 0.2 mm). The dry product (109C) weighed 2.5261 g (167%).

Reaction of Acetylated Preasphaltene C-22440 with Pyridine Hydriodide: The acetylated preasphaltene (0.6836 g), pyridine hydriodide (0.4219 g) and 60 mL of pyridine (distilled from BaO) were heated at an oil bath temperature of 58° for 6 days under nitrogen. The reaction mixture was cooled, added to 400 mL of 10% HCl, stirred overnight and vacuum filtered. The precipitate was washed with water (3 X 150 mL) and dried in an Abderhalden apparatus (100°, 0.2 mm) to give 0.5801 g (84.85%) of product (110): 5.31 mmoL phenol g^{-1}.

TABLE 4*

GC QUANTITATIVE ANALYSIS OF ACETYLATION OF PHENOL WITH PYRIDINE AND ACETIC ANHYDRIDE

Standard Solutions:
Component = Phenyl Acetate (i)
Internal Standard = Benzyl acetate (s)
Slope = 1.10; y Intercept = .0889
Correlation Coefficient = 1.00

HT_i**	HT_s	HT_i/HT_s	W_i	W_s	W_i/W_s
71.2	48.5	1.47	1.0656	.8560	1.245
60.5	54.9	1.10	.8927	.9713	.9191
75.4	44.5	1.69	1.2960	.8896	1.457
84.8	47.3	1.79	1.4029	.9086	1.544
50.7	50.2	1.01	.7463	.8916	.8370

Solution Under Analysis:

HT_i	HT_s	HT_i/HT_s	W_s	W_i (expt)***
96.3	59.5	1.62	.8965	1.24

*Page 25 of experimental section.
**HT = peak height; for discussion of this method, see Ball,D.L. and Harris,W.E., Anal Chem,1968,40(129-34).
***Sample was 77.86% of the reaction mixture.

TABLE 5*

GC QUANTITATIVE ANALYSIS OF THE REACTION FOR ACETYLATION OF PHENOLS APPLIED TO PHENYL PHENETHYL ETHER

Standard Solutions:
Component = Phenyl Phenethyl Ether (i)
Internal Standard = Phenyl Ether (s)
Slope = 1.06; y Intercept = -.0634
Correlation coefficient = .986

A_i	A_s	A_i/A_s	W_i	W_s	W_i/W_s
97.1	92.5	1.05	.1460	.1479	.987
48.5	81.0	.592	.0964	.1493	.646
110	141	.780	.1559	.1988	.784
104	85.0	1.22	.1970	.1588	1.24

Solution Under Analysis:

A_i	A_s	A_i/A_s	W_s	W_i (expt)**
83.0	109	.761	.5078	.393

*Page 27 of experimental section.
**Sample was 24.48% of the reaction mixture.

TABLE 6

*GC QUANTITATIVE ANALYSIS OF DETERMINATIVE REACTION OF FERRIC CHLORIDE/ ACETIC ANHYDRIDE WITH BENZYL PHENYL ETHER (3h,rt)

Standard Solutions:
Component = Phenyl Acetate (i)
Internal Standard = Biphenyl (s)
Slope = 1.06
y Intercept = -.00438
Correlation Coefficient = .989

A_i/A_s	W_i	W_s	W_i/W_s
.281	.0477	.1859	.257
.304	.0544	.1788	.304
.509	.0852	.1815	.469
.455	.0757	.1697	.446

Solution Under Analysis:

A_i	A_s	A_i/A_s	W_s	W_i(expt)
3.4	35.6	.096	.6407	.0604

Standard Solutions:
Component = Benzyl Acetate (i)
Internal Standard = Biphenyl (s)
Slope = 1.01
y Intercept = .0241
Correlation Coefficient = .985

A_i/A_s	W_i	W_s	W_i/W_s
.252	.0382	.1859	.205
.282	.0515	.1788	.288
.518	.0881	.1815	.485
.457	.0722	.1697	.425

Solution Under Analysis:

A_i	A_s	A_i/A_s	W_s	W_i(expt)
3.6	26.1	.14	.6407	.074

*Page 28 of experimental section.

TABLE 7

*GC QUANTITATIVE ANALYSIS OF TWO DETERMINATIVE REACTIONS OF FERRIC CHLORIDE/ ACETIC ANHYDRIDE WITH BENZYL PHENYL ETHER (80°, 24h and 77°, 3h)

Standard Solutions:
Component = Phenyl Acetate (i)
Internal Standard = Biphenyl (s)
Slope = 1.08; y Intercept = -.00374
Correlation Coefficient = 1.00

A_i	A_s	A_i/A_s	W_i	W_s	W_i/W_s
46.2	63.7	.725	.0534	.0797	.670
48.1	86.0	.559	.0906	.1722	.526
27.5	77.5	.355	.0534	.1621	.329

Solution Under Analysis:
(page 30, 24h, 80°)

A_i	A_s	A_i/A_s	W_s	W_i (expt)
54.7	81.0	.675	.9519	.597

Solution Under Analysis:
(page 29, 3h, 77°)

A_i	A_s	A_i/A_s	W_s	W_i (expt)
46.2	102.3	.452	.9861	.415

Standard Solutions:
Component = Benzyl Acetate (i)
Internal Standard = Biphenyl (s)
Slope = 1.15; y Intercept = -.0409
Correlation Coefficient = .995

A_i	A_s	A_i/A_s	W_i	W_s	W_i/W_s
33.8	63.7	.531	.0386	.0797	.484
47.2	86.0	.549	.0901	.1722	.523
23.5	77.5	.303	.0488	.1621	.301

Solution Under Anlysis:
(page 30, 24h, 80°)

A_i	A_s	A_i/A_s	W_s	W_i (expt)
37.5	81.0	.463	.9519	.417

Solution Under Analysis:
(page 29, 3h, 77°)

A_i	A_s	A_i/A_s	W_s	W_i (expt)
38.1	102.3	.372	.9861	.354

*Pages 29 and 30 of experimental section.

TABLE 8

*GC QUANTITATIVE ANALYSIS OF THE REACTION OF FERRIC CHLORIDE/ ACETIC ANHYDRIDE WITH PHENOL

Standard Solutions:

Component = Phenyl Acetate (i)
Internal Standard = Benzyl Acetate (s)
Slope = .950; y Intercept = .0764
Correlation Coefficient = .998

A_i/A_s	W_i	W_s	W_i/W_s
1.12	.1780	.1753	1.105
.731	.2794	.4079	.6850
.760	.1751	.2504	.6993
.584	.1582	.2864	.5524

Solution Under Analysis:

A_i/A_s	W_s	W_i (expt)
.596	1.1198	0.613**

*Page 30 of experimental section.
**Sample was 13.70% of the reaction mixture.

TABLE 9

*HPLC QUANTITATIVE ANALYSIS OF THE REACTION OF FERRIC CHLORIDE/ ACETIC ANHYDRIDE (1h,25°) WITH BENZYL PHENYL ETHER

Solution Under Analysis:

Component = Phenyl Acetate (i)
Internal Standard = Chlorobenzene (s)
Slope = 1.24; y Intercept = .00194

A_i	A_s	A_i/A_s	W_s	W_i (expt)**
11806	57462	.205	.1695	.0274

Component = Benzyl Phenyl Ether (i)
Internal Standard = Chlorobenzene (s)
Slope = 3.02; y Intercept = −.0320
Correlation Coefficient = 1.00

A_i	A_s	A_i/A_s	W_s	W_i (expt)**
52784	13074	4.04	.1695	.228

Component = p-Benzyloxyacetophenone (i)
Internal Standard = Biphenyl (s)
Slope = .366; y Intercept = .0762
Correlation Coefficient = .999

A_i	A_s	A_i/A_s	W_s	W_i (expt)**
17395	47966	.363	.0137	.0108

*Slopes and intercepts are from the standard solutions in Table 10.
**Sample was 40% of the reaction mixture.

TABLE 10

*HPLC QUANTITATIVE ANALYSIS OF THE REACTION OF FERRIC CHLORIDE/ ACETIC ANHYDRIDE WITH BENZYL PHENYL ETHER (3h, 77°)

Standard Solutions:
Component = Benzyl Phenyl Ether (i)
Internal Standard = Chlorobenzene (s)
Slope = 3.02
y Intercept = -.0320
Correlation Coefficient = 1.00

A_i	A_s	A_i/A_s	W_i	W_s	W_i/W_s
14916	21432	.696	.0101	.0419	.241
15985	22956	.696	.0101	.0419	.241
21057	14859	1.42	.0152	.0314	.484
20866	14455	1.44	.0152	.0314	.484

Solution Under Analysis:

A_i	A_s	A_i/A_s	W_s	W_i (expt)**
6617	48398	.137	.1244	.00697

Standard Solutions:
Component = Phenyl Acetate (i)***
Internal Standard = Chlorobenzene (s)
Slope = 1.24
y Intercept = .00194
Correlation Coefficient = .998

A_i	A_s	A_i/A_s	W_i	W_s	W_i/W_s
15174	21432	.708	.0239	.0419	.588
16434	22956	.716	.0239	.0419	.588
10609	14859	.714	.0175	.0314	.559
10345	14455	.715	.0175	.0314	.559

Solution Under Analysis:

A_i	A_s	A_i/A_s	W_s	W_i (expt)**
45885	48398	.948	.1244	.0950

TABLE 10 CONTINUED ON FOLLOWING PAGE

*Page 32 of experimental section.
**Sample was 40% of the reaction mixture
***Due to the proximity of the two sets of points, 0,0 was used as an additional point in the data.

TABLE 10 (CON'T)

Standard Solutions:
Component = p-Acetoxyacetophenone (i)
Internal Standard = Chlorobenzene (s)
Slope = 46.7
y Intercept = .220
Correlation Coefficient = .952

A_i	A_s	A_i/A_s	W_i	W_s	W_i/W_s
73424	48417	1.52	.000168	.00548	.0306
86596	48743	1.78	.000168	.00548	.0306
54495	50611	1.08	.000103	.00559	.0184
57621	53465	1.08	.000103	.00559	.0184

Solution Under Analysis:

A_i	A_s	A_i/A_s	W_s	W_i(expt)*
34599	48398	.715	.1244	1.32×10^{-3}

Standard Solutions:
Component = p-Benzyloxyacetophenone (i)
Internal Standard = Biphenyl (s)
Slope = .366
y Intercept = .0762
Correlation Coefficient = .999

A_i	A_s	A_i/A_s	W_i	W_s	W_i/W_s
151291	108971	1.39	.00147	.000405	3.63
140577	99190	1.42	.00147	.000405	3.63
116302	143439	.811	.00105	.000520	2.01
87780	108014	.813	.00105	.000520	2.01

Solution Under Analysis:

A_i	A_s	A_i/A_s	W_s	W_i(expt)*
119838	137261	.873	.0242	.0527

*Sample was 40% of the reaction mixture

TABLE 11

*HPLC QUANTITATIVE ANALYSIS OF THE REACTION OF FERRIC CHLORIDE/ ACETIC ANHYDRIDE WITH BUTYL PHENYL ETHER

Standard Solutions:
Component = Butyl Phenyl Ether (i)
Internal Standard = Bibenzyl (s)
Slope = 1.19
y Intercept = .111
Correlation Coefficient = 1.00

A_i	A_s	A_i/A_s	W_i	W_s	W_i/W_s
333910	197922	1.68	.01536	.01158	1.33
325996	191286	1.70	.01536	.01158	1.33
198929	220543	.901	.01024	.01544	.663
275106	307375	.895	.01024	.01544	.663

Solution Under Analysis:

A_i	A_s	A_i/A_s	W_s	W_i (expt)**
65592	72508	.905	.0382	.0255

Standard Solutions:
Component = p-Butoxyacetophenone (i)
Internal Standard = Acetophenone (s)
Slope = 1.55
y Intercept = .196
Correlation Coefficient = 1.00

A_i	A_s	A_i/A_s	W_i	W_s	W_i/W_s
148639	84283	1.76	.01044	.01039	1.01
141354	80242	1.76	.01044	.01039	1.01
41878	43028	.973	.00696	.01386	.502
22204	22784	.974	.00696	.01386	.502

Solution Under Analysis:

A_i	A_s	A_i/A_s	W_s	W_i (expt)***
101515	49225	2.06	.1268	.152

*Page 35 of experimental section.
**Sample was 40% of the reaction mixture.
***Sample was 20% of the reaction mixture.

TABLE 12
*HPLC QUANTITATIVE ANALYSIS OF THE REACTION OF FERRIC CHLORIDE/ ACETIC ANHYDRIDE WITH 2-NAPHTHYL BENZYL ETHER

Standard Solutions:
Component = 2-Naphthyl Acetate (i)
Internal Standard = Naphthalene (s)
Slope = .814
y Intercept = .00763
Correlation Coefficient = 1.00

A_i	A_s	A_i/A_s	W_i	W_s	W_i/W_s
169078	120408	1.40	.0929	.0537	1.73
184732	129038	1.43	.0929	.0537	1.73
148908	210047	.709	.0929	.107	.864
185328	260094	.712	.0929	.107	.864

Solution Under Analysis:

A_i	A_s	A_i/A_s	W_s	W_i (expt)**
280515	310104	.904	.0537	.0591

Standard Solutions:
Component = 2-Naphthyl Benzyl Ether (i)
Internal Standard = Naphthalene (s)
Slope = .692
y Intercept = .0106
Correlation Coefficient = 1.00

A_i	A_s	A_i/A_s	W_i	W_s	W_i/W_s
156068	120408	1.30	.1005	.0537	1.87
168603	129038	1.31	.1005	.0537	1.87
137556	210047	.655	.1005	.107	.936
172287	260094	.662	.1005	.107	.936

Solution Under Analysis:

A_i	A_s	A_i/A_s	W_s	W_i (expt)**
125506	310104	.404	.0537	.0305

*Page 36 of experimental section.
**Sample was 20% of the reaction mixture.

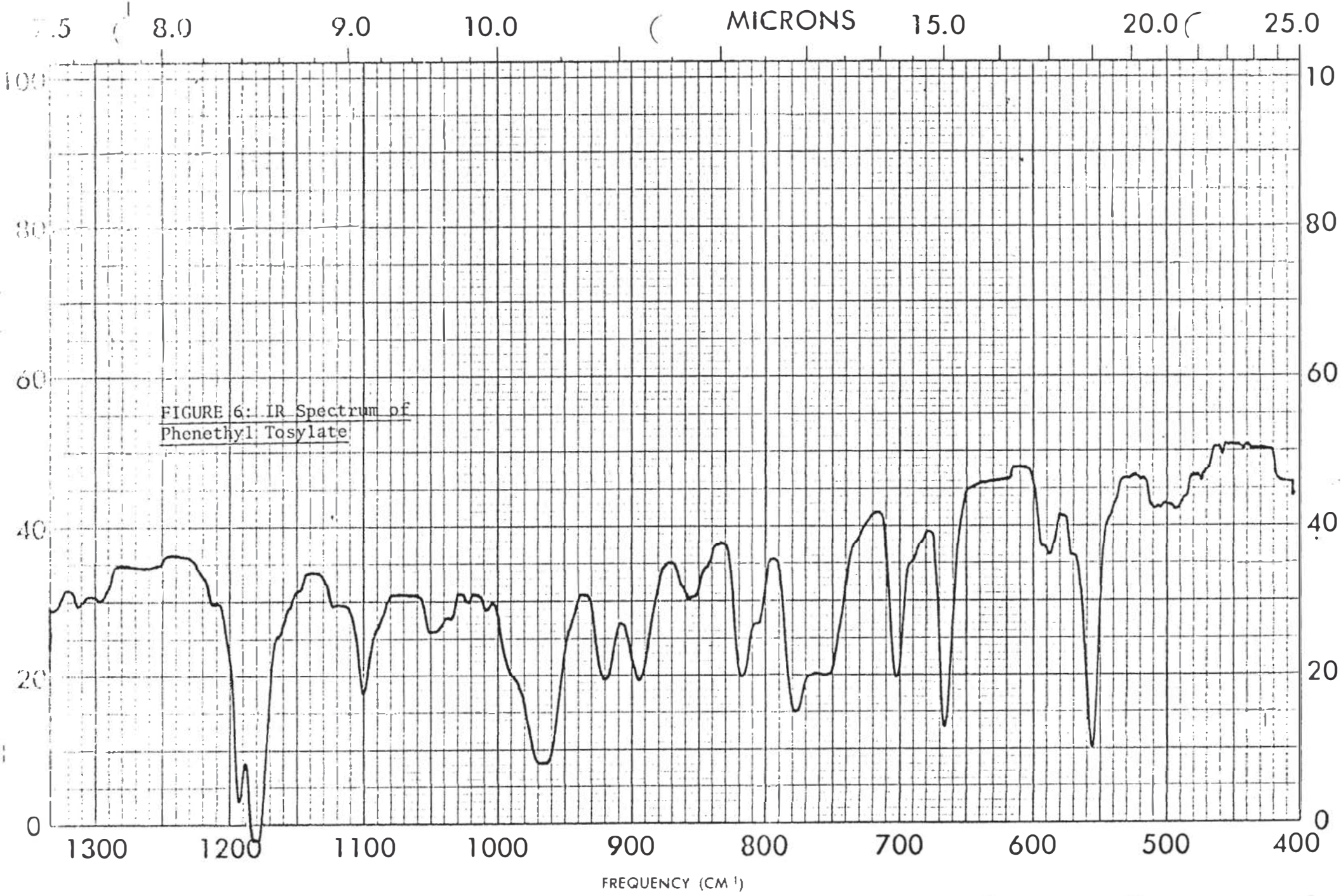


FIGURE 6: IR Spectrum of Phenethyl Tosylate

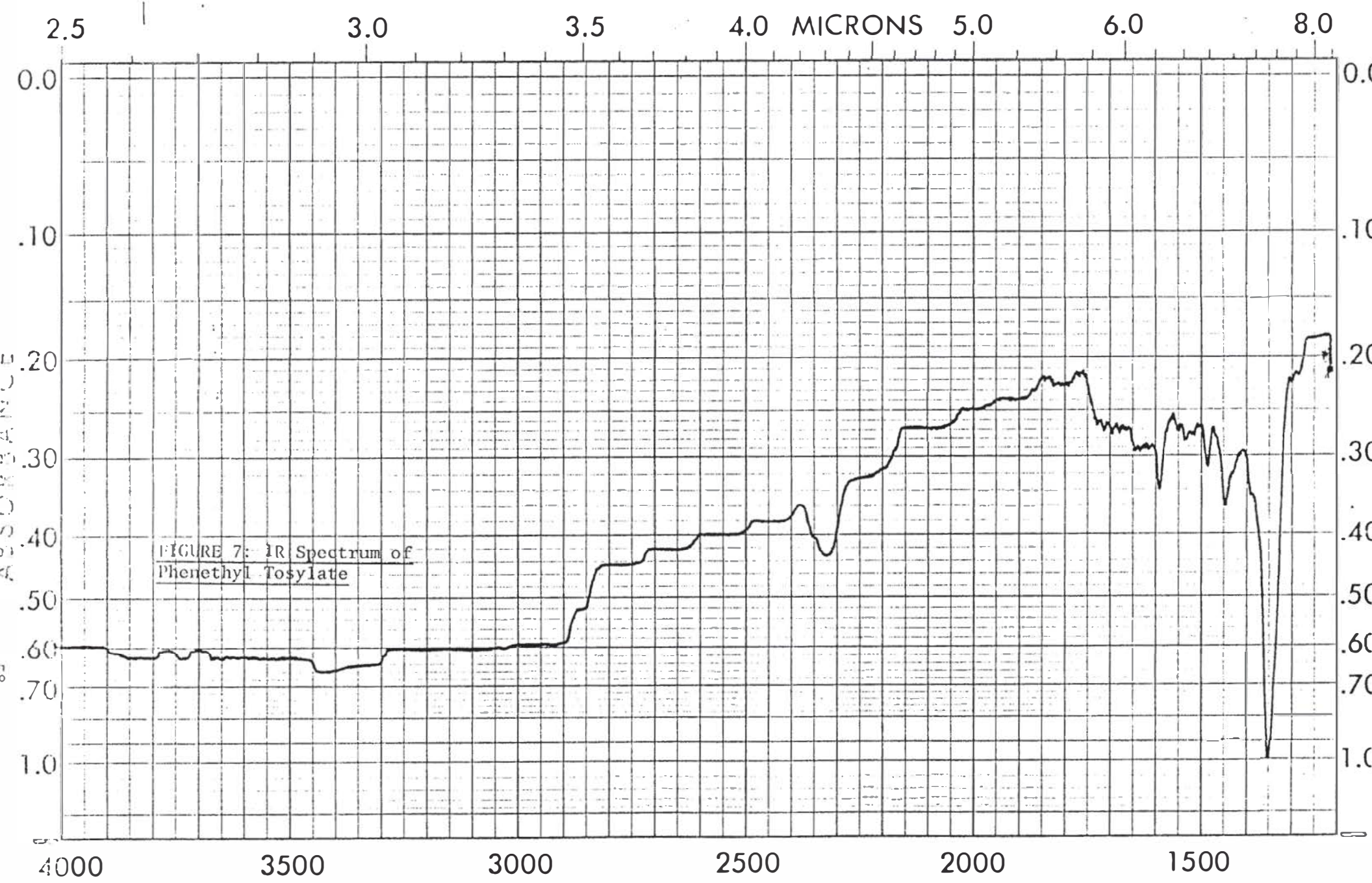


FIGURE 7: IR Spectrum of Phenethyl Tosylate

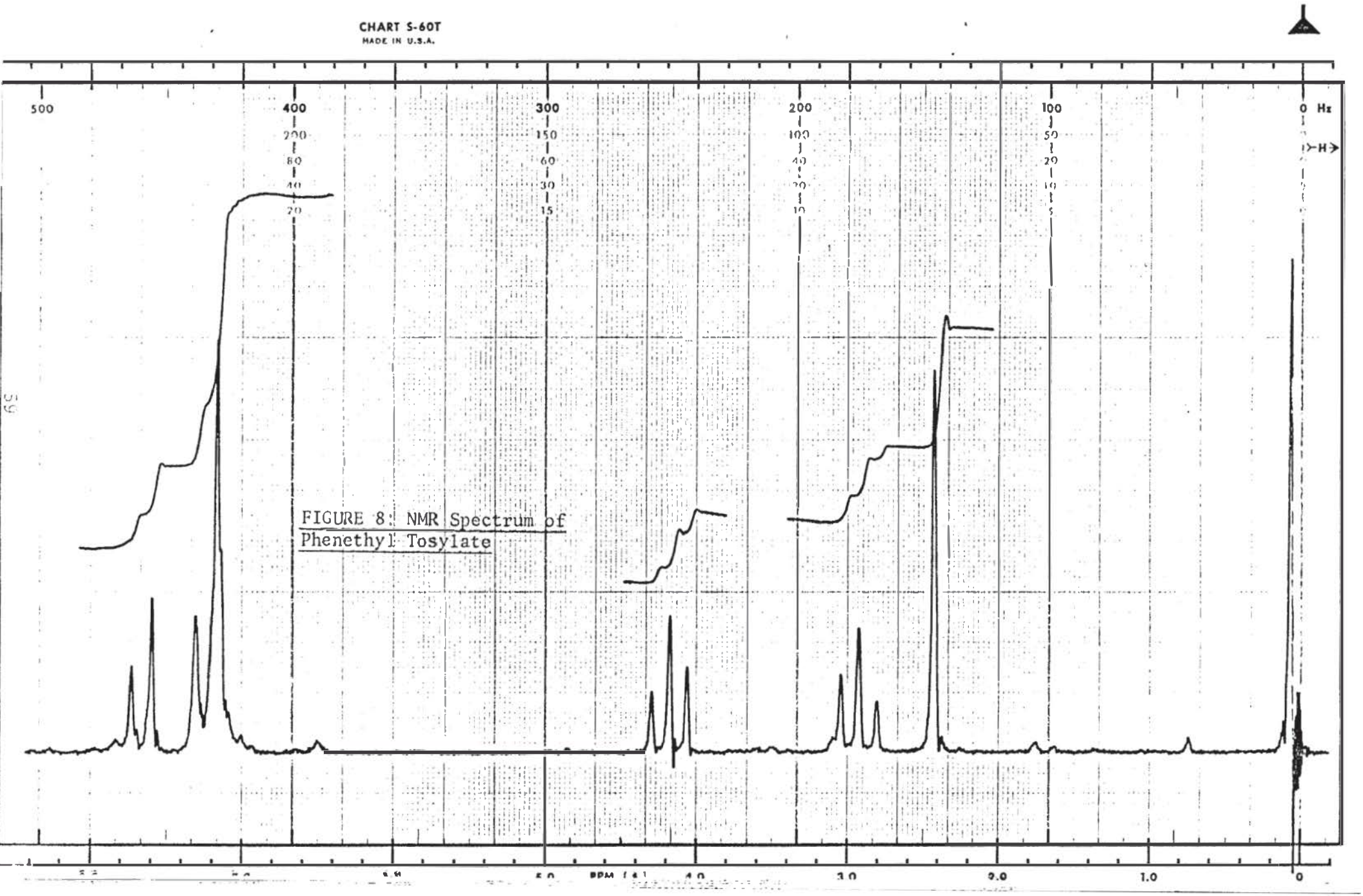


FIGURE 8: NMR Spectrum of Phenethyl Tosylate

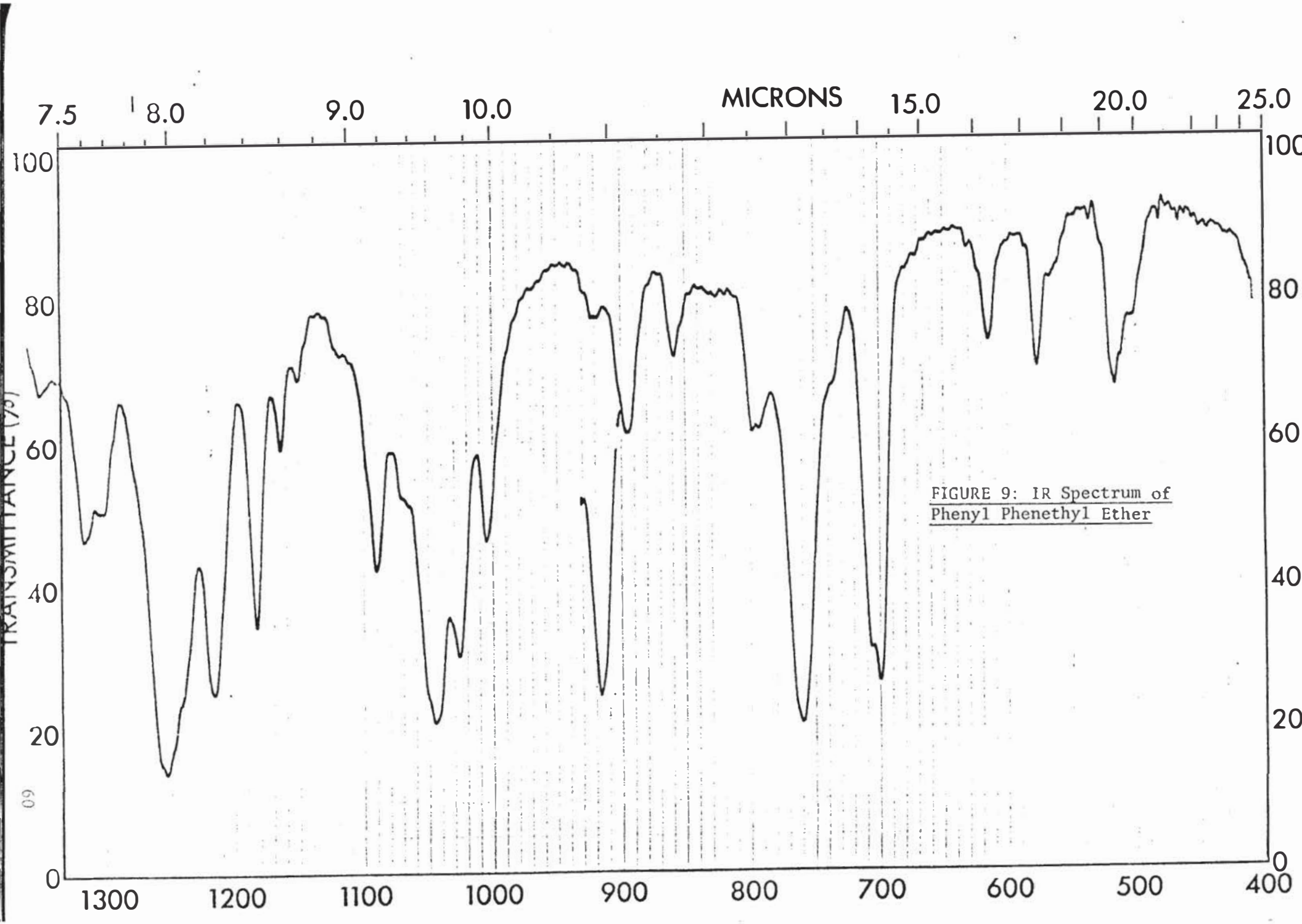


FIGURE 9: IR Spectrum of Phenyl Phenethyl Ether

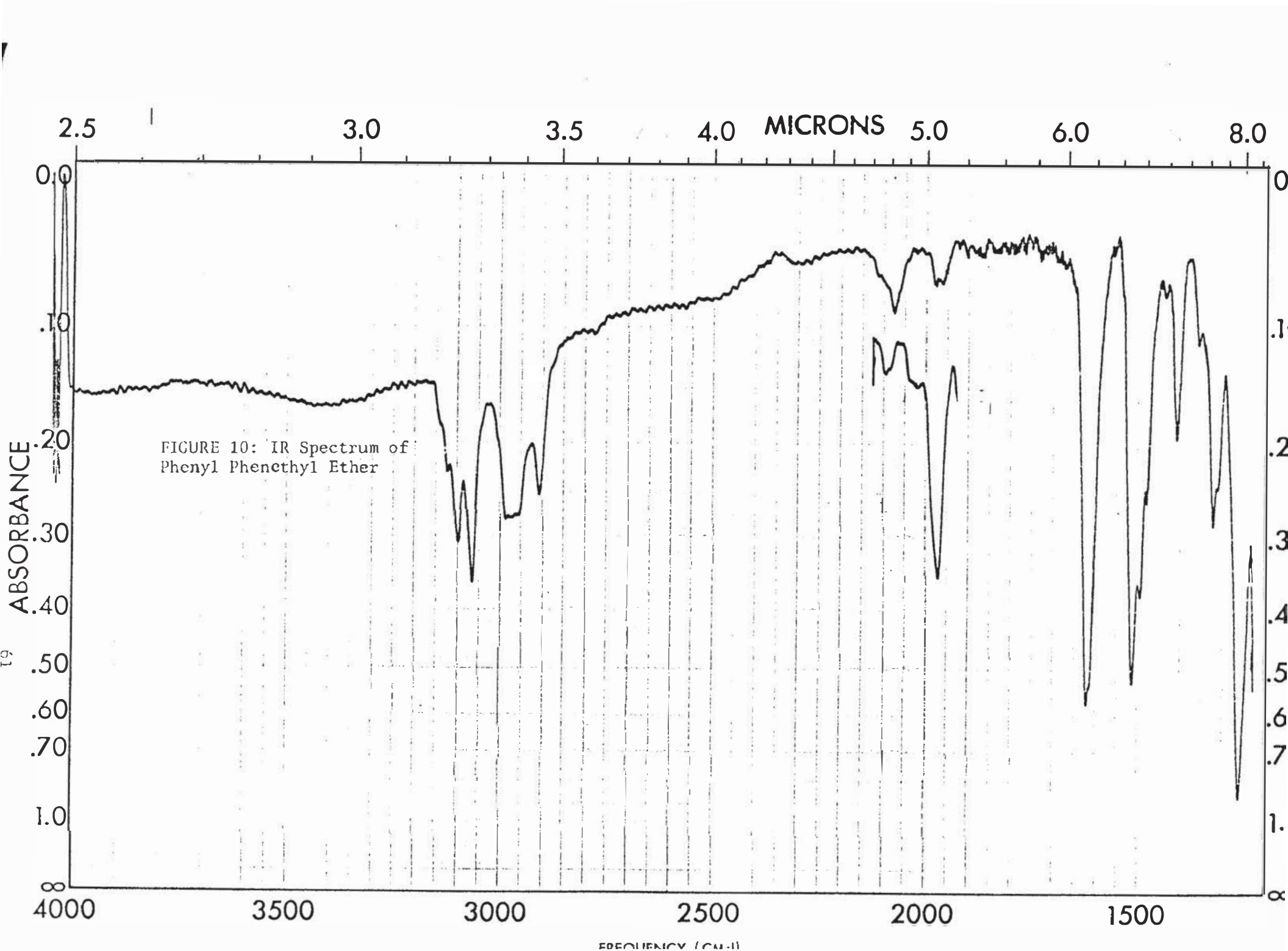


FIGURE 10: IR Spectrum of Phenyl Phenethyl Ether

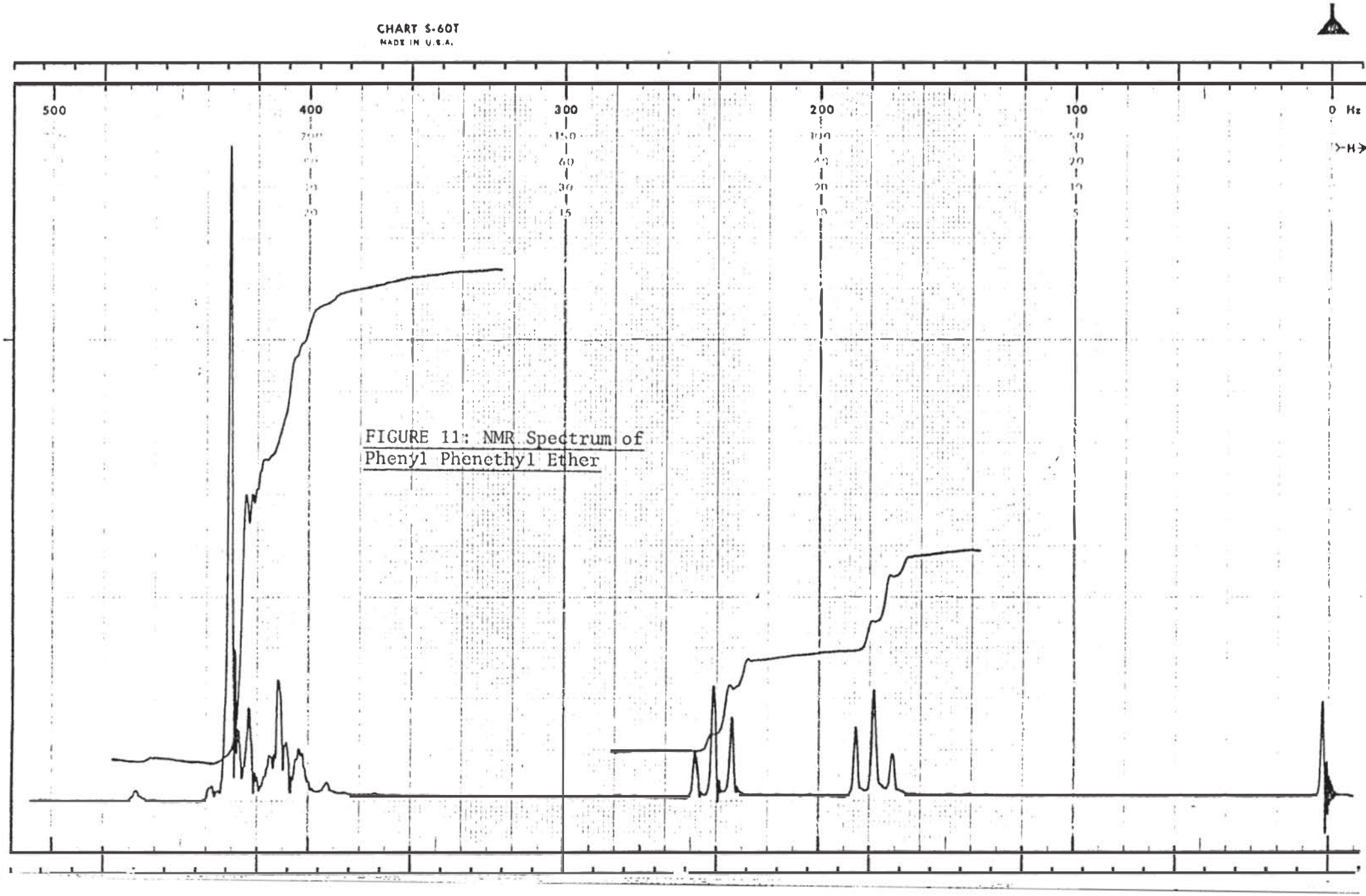


FIGURE 11: NMR Spectrum of
Phenyl Phenethyl Ether

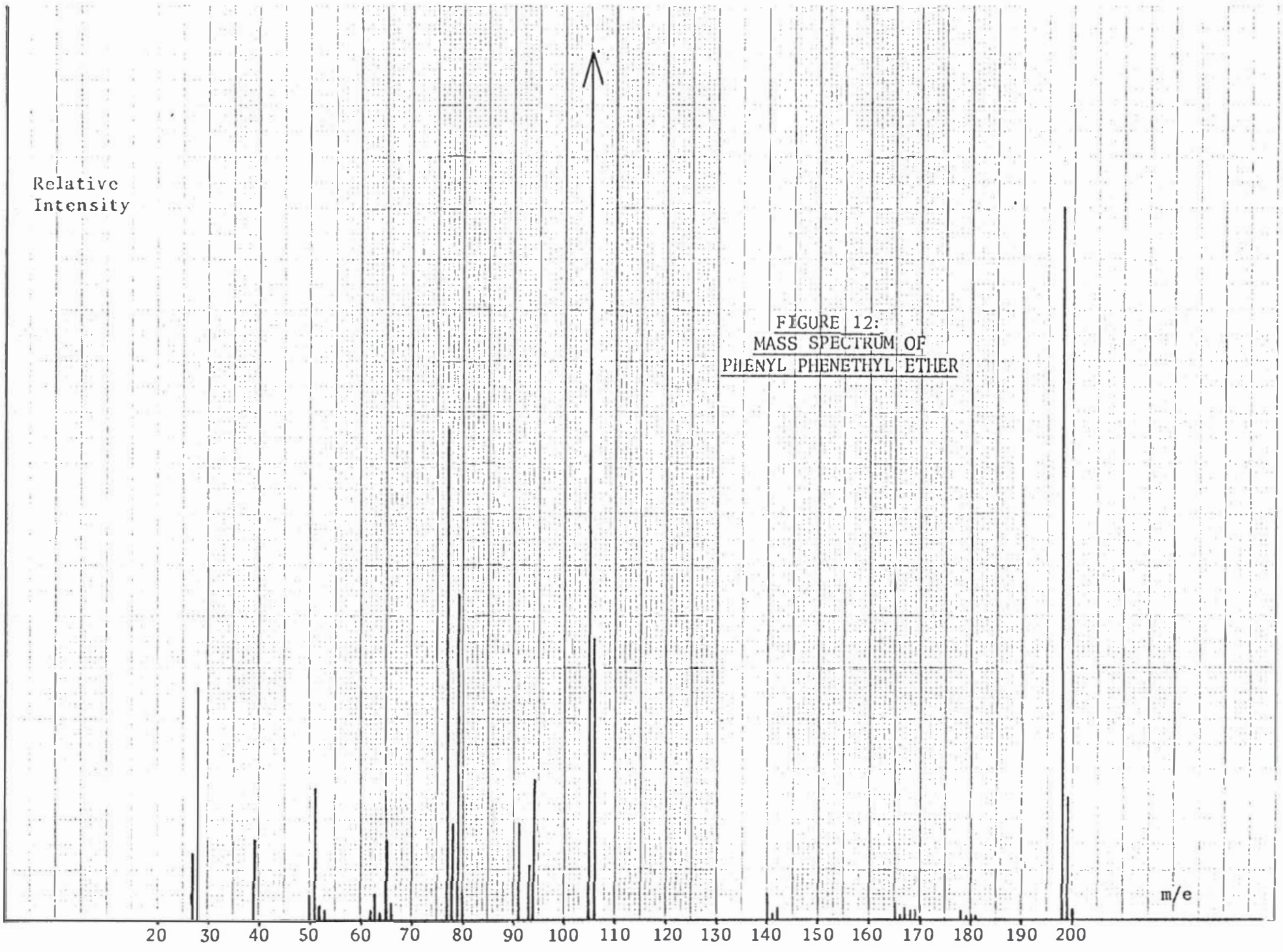


FIGURE 12:
MASS SPECTRUM OF
PHENYL PHENETHYL ETHER

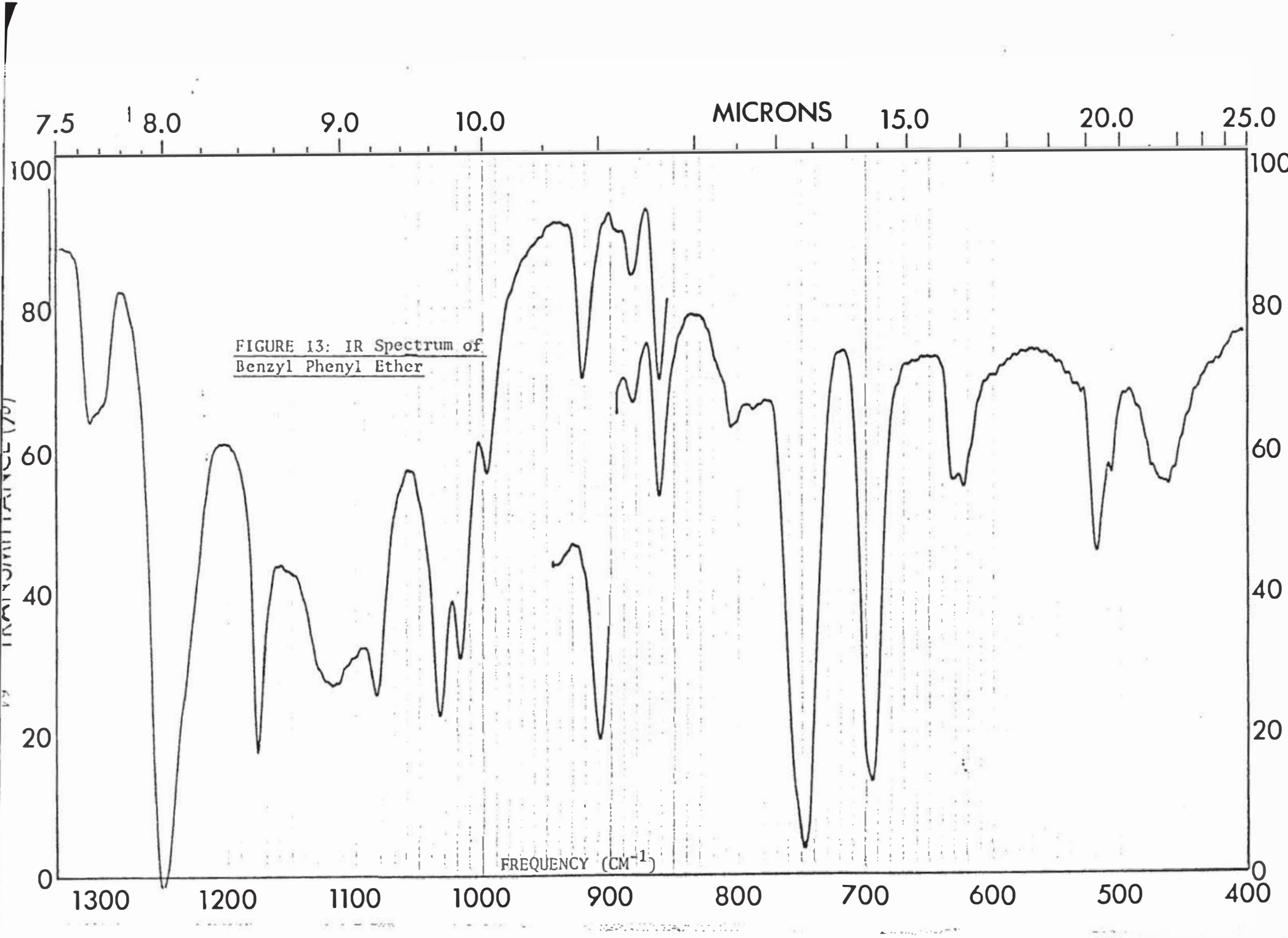


FIGURE 13: IR Spectrum of Benzyl Phenyl Ether

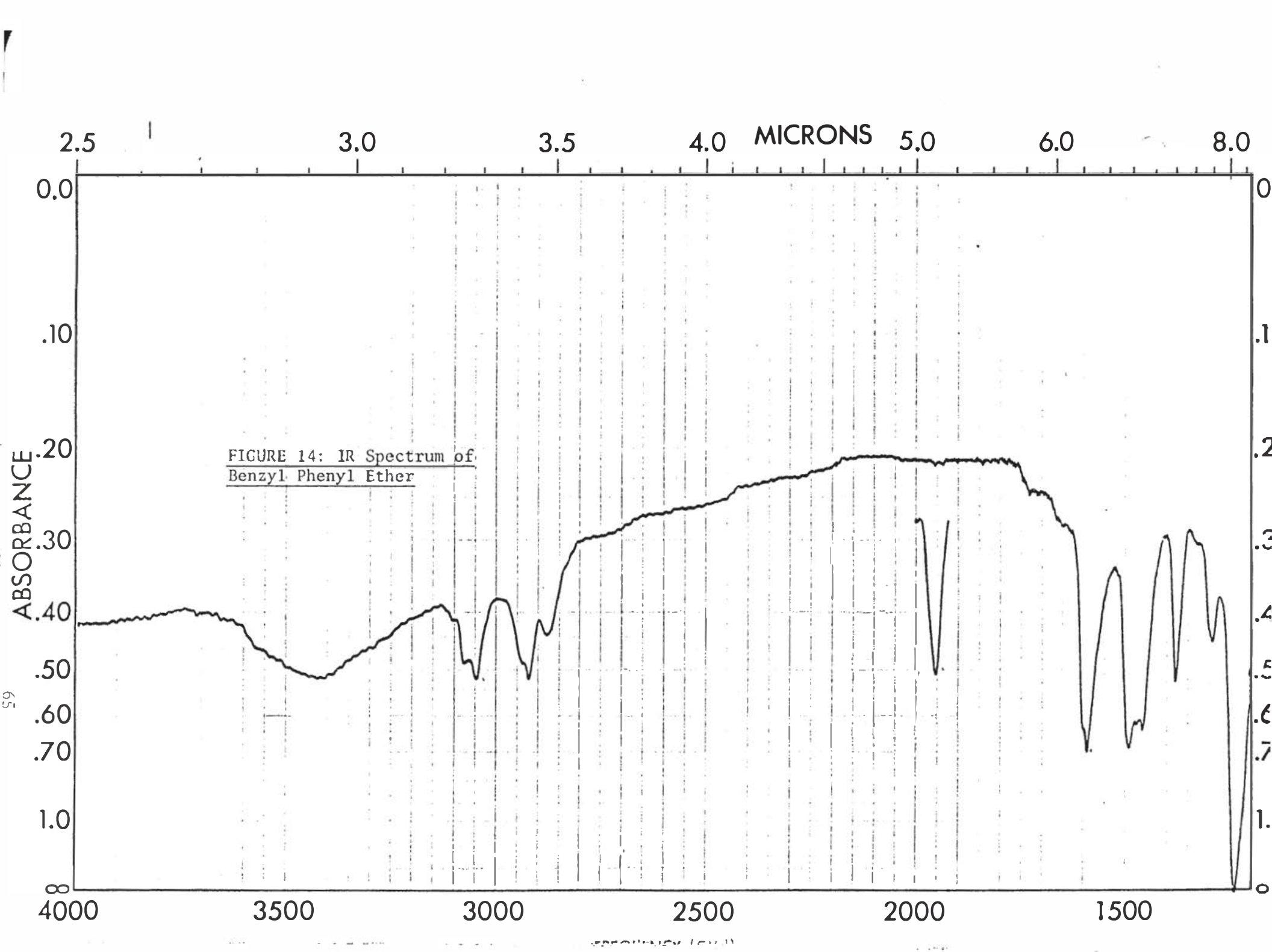


FIGURE 14: IR Spectrum of Benzyl Phenyl Ether

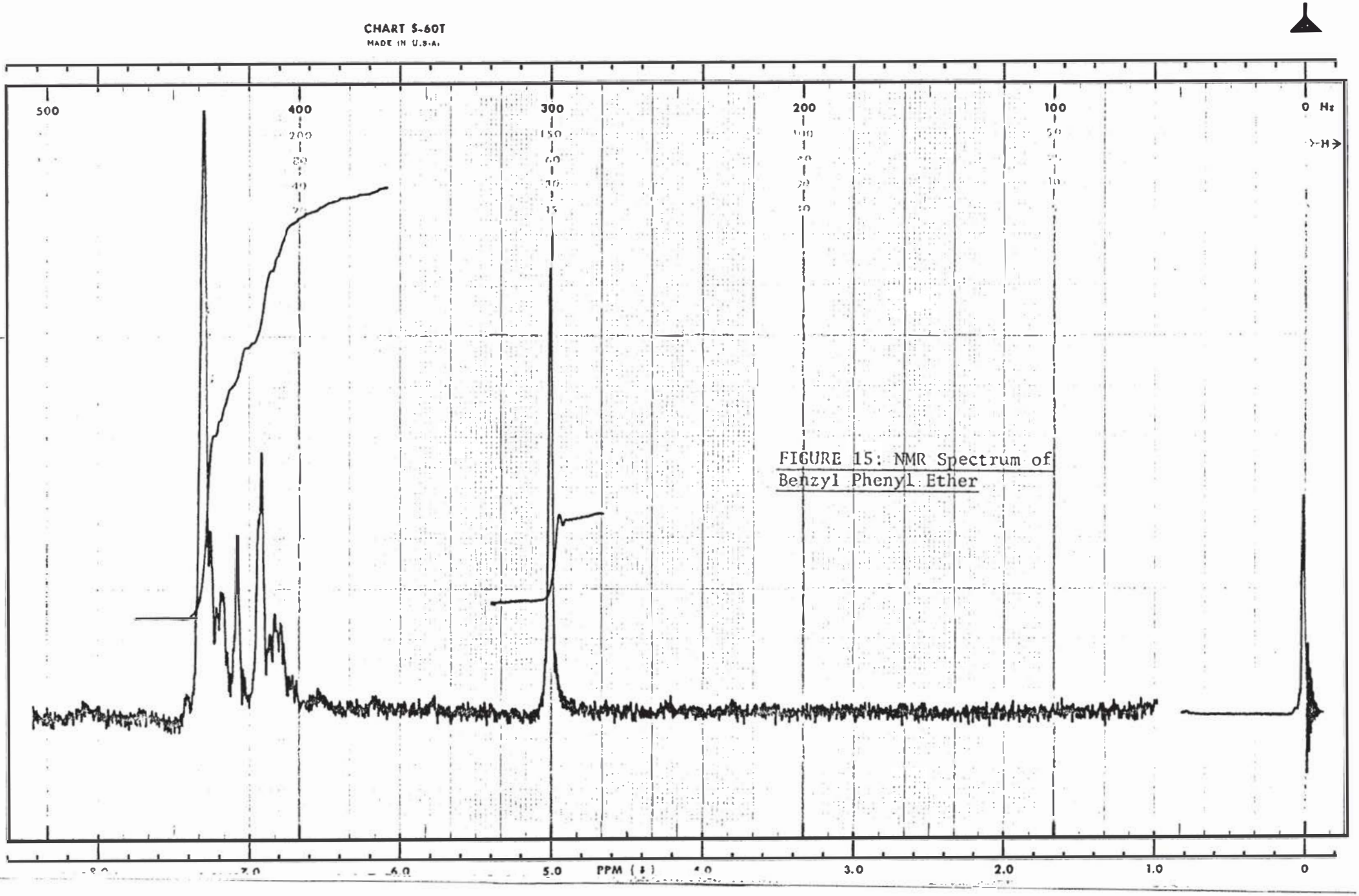


FIGURE 15: NMR Spectrum of Benzyl Phenyl Ether

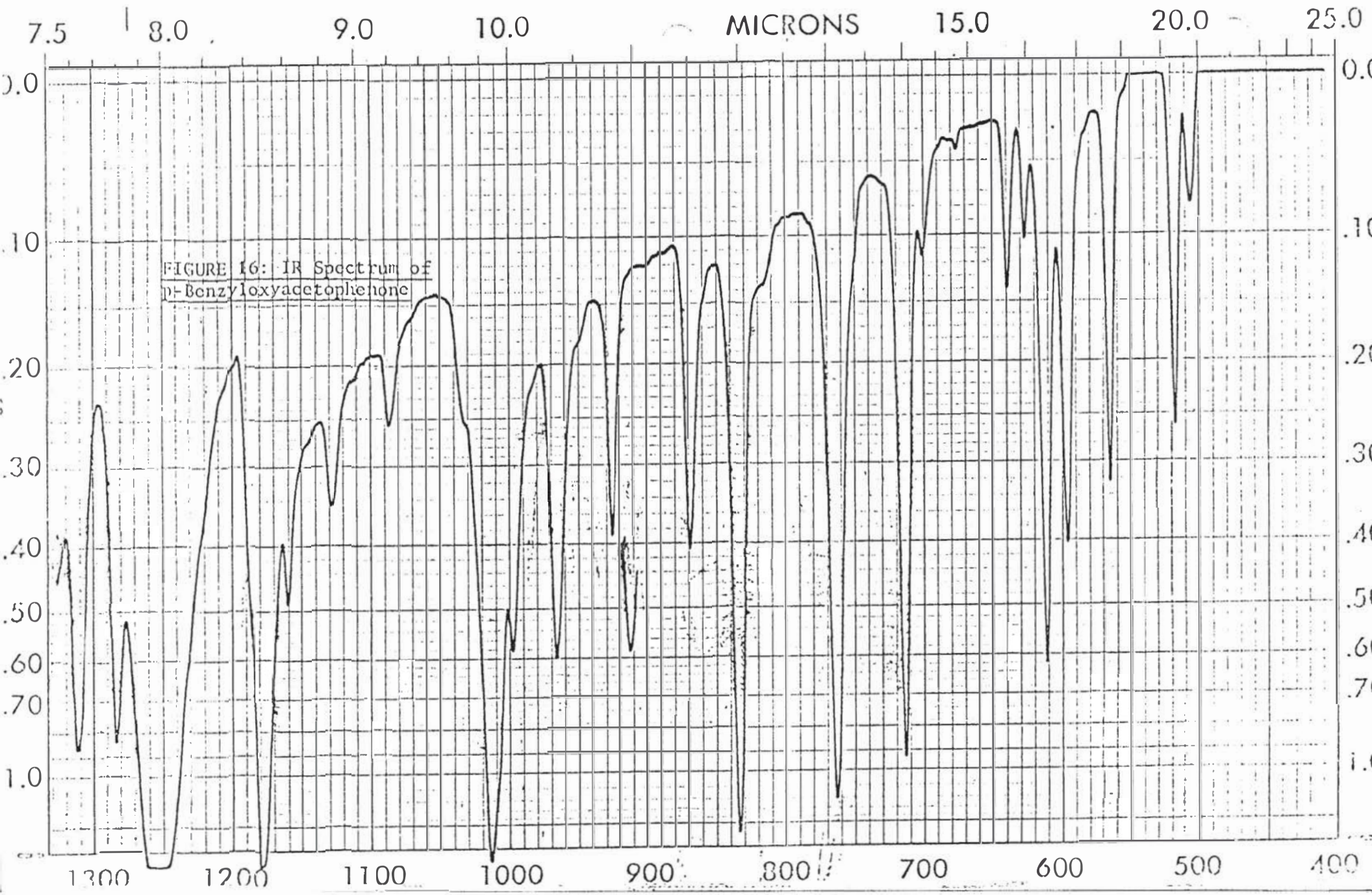


FIGURE 16: IR Spectrum of p-Benzyloxyacetophenone

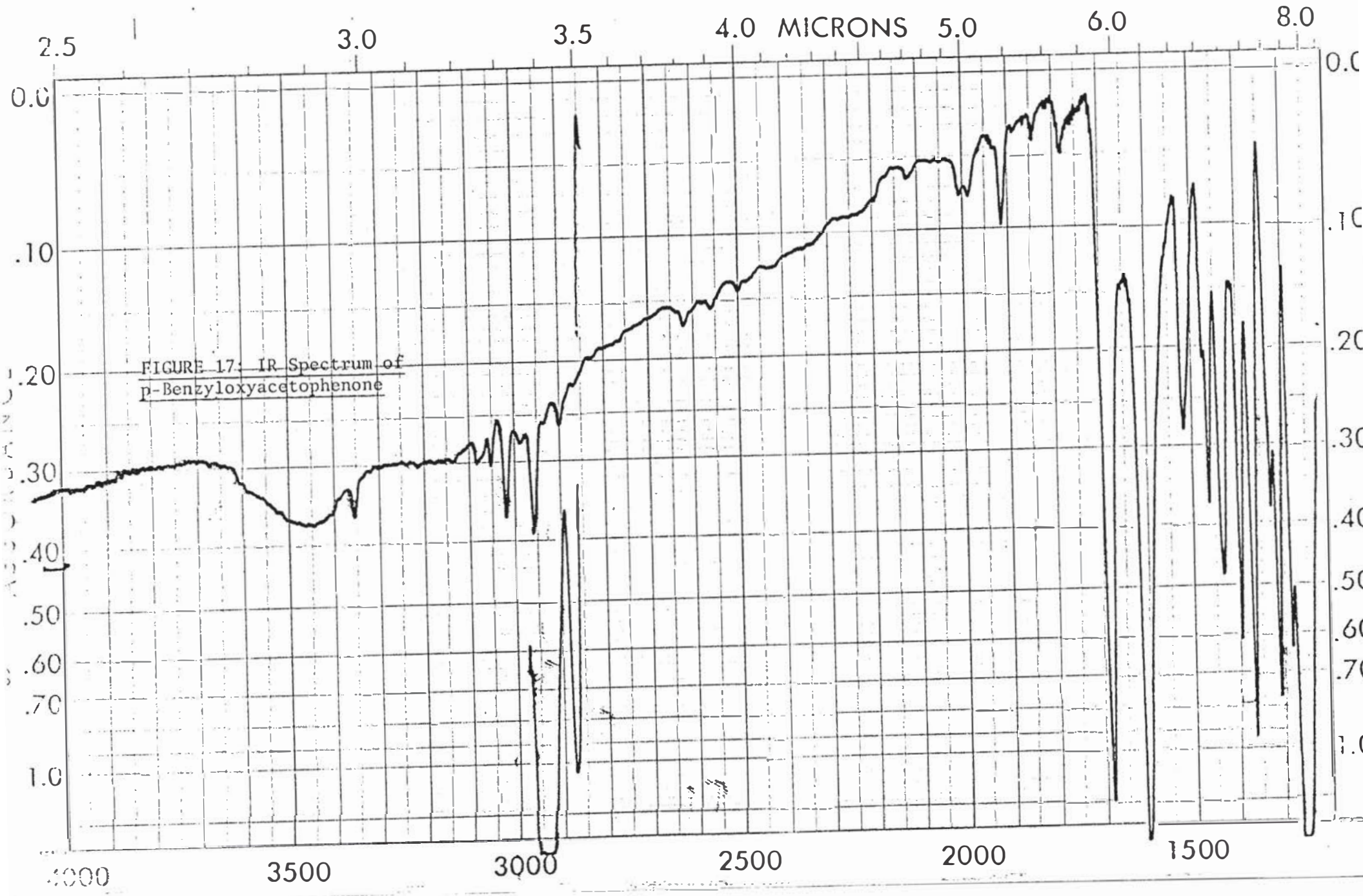


FIGURE 17: IR Spectrum of p-Benzyloxyacetophenone

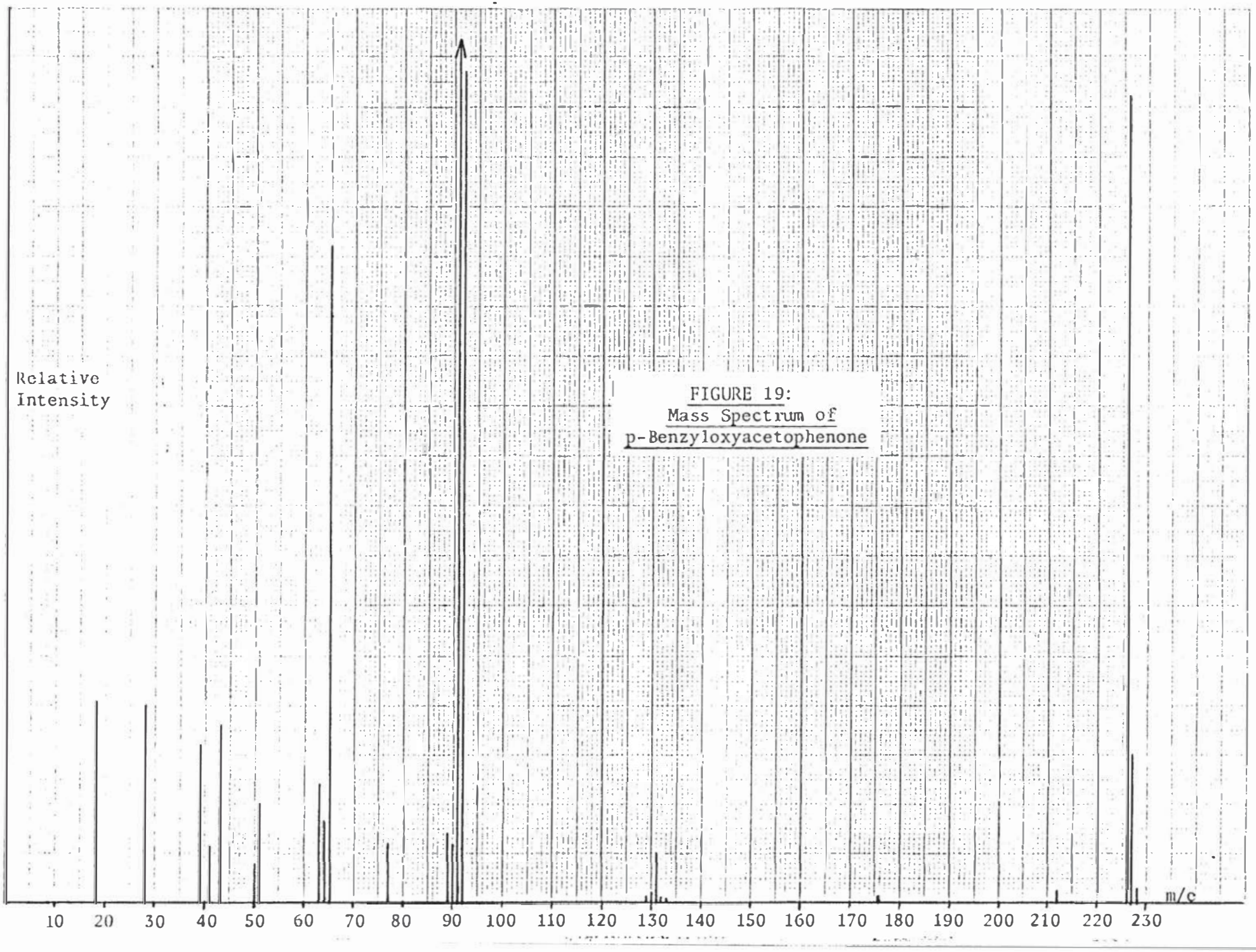


FIGURE 19:
Mass Spectrum of
p-Benzyloxyacetophenone

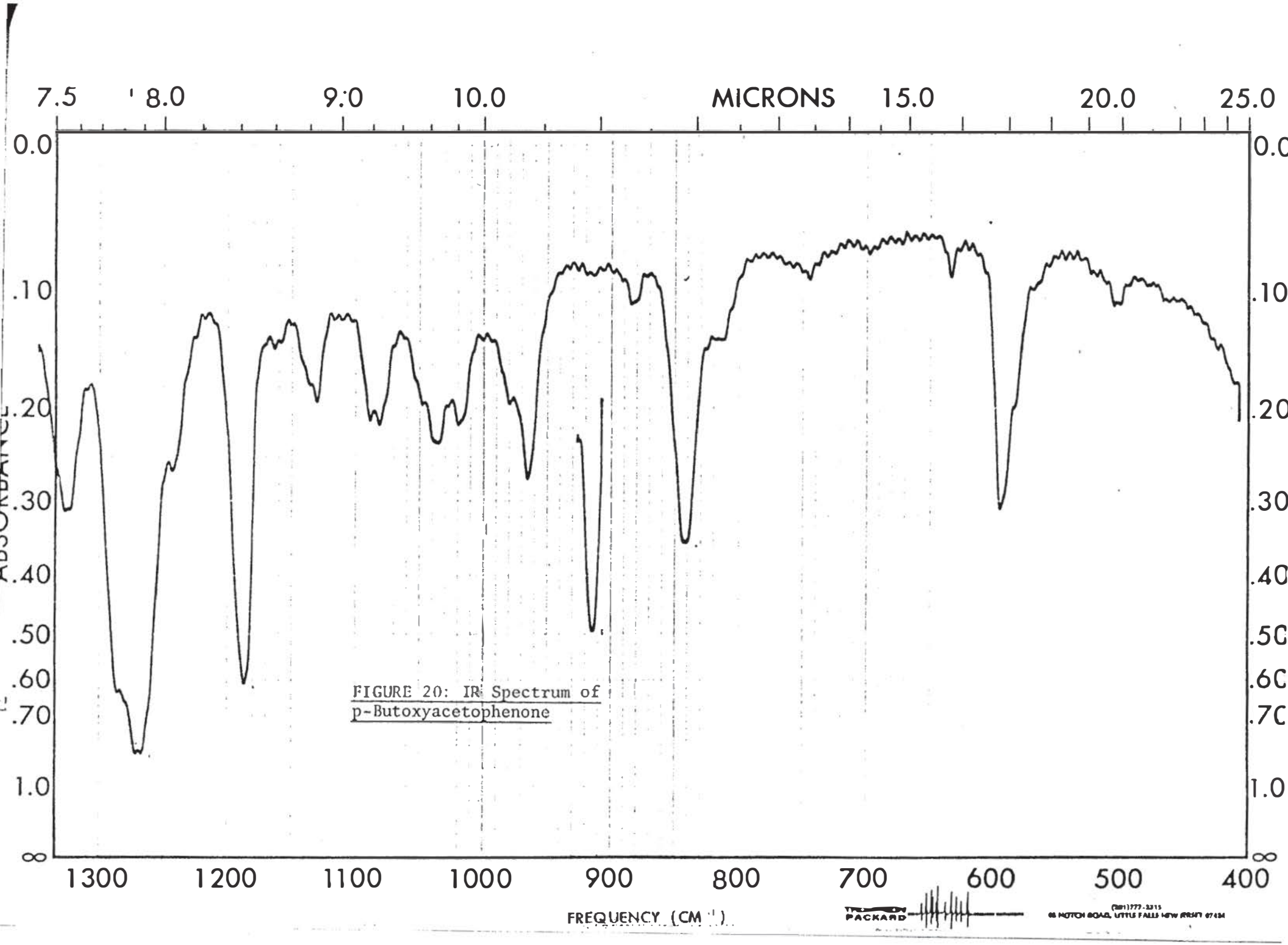


FIGURE 20: IR Spectrum of p-Butoxyacetophenone

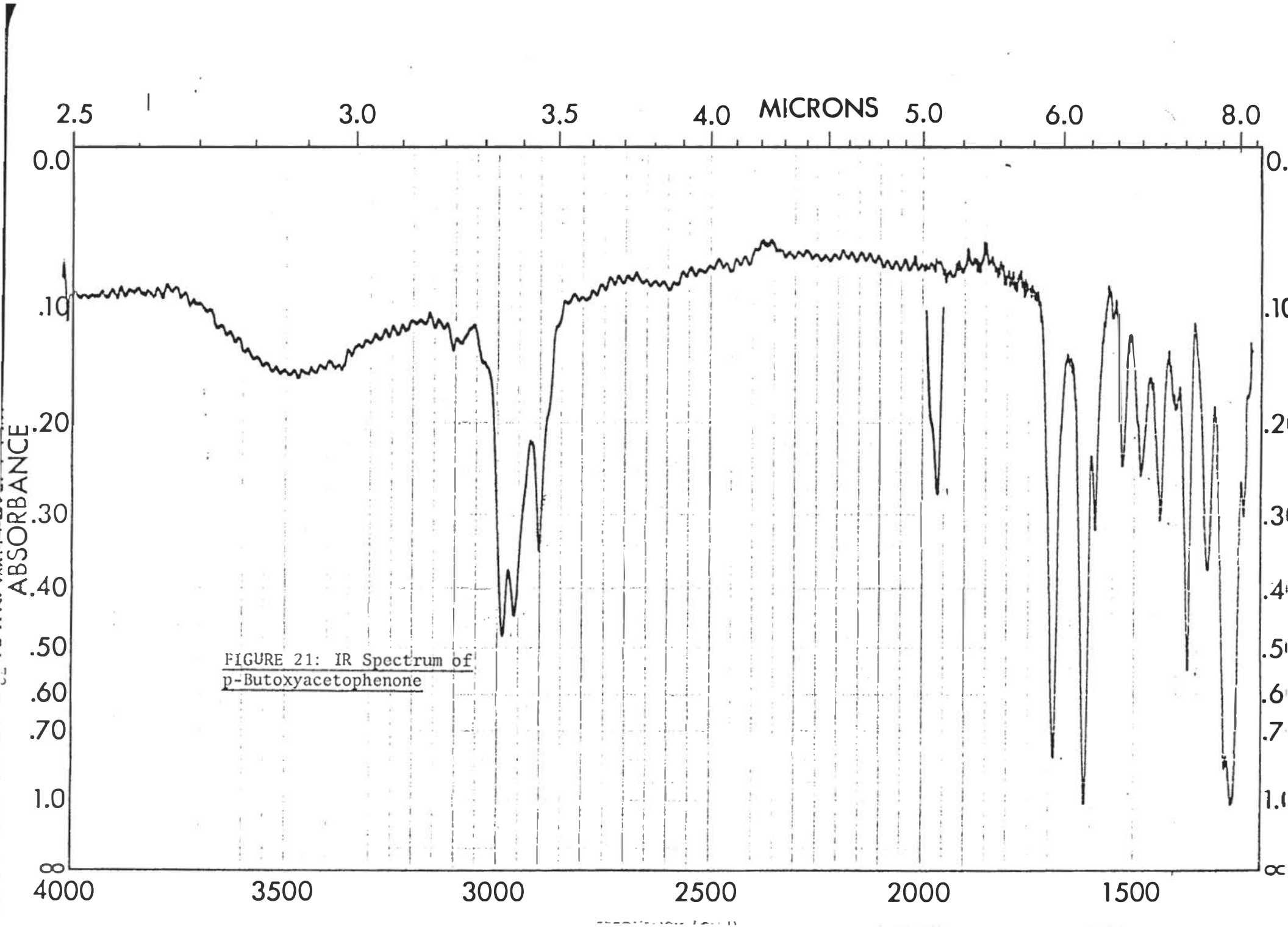


FIGURE 21: IR Spectrum of p-Butoxyacetophenone

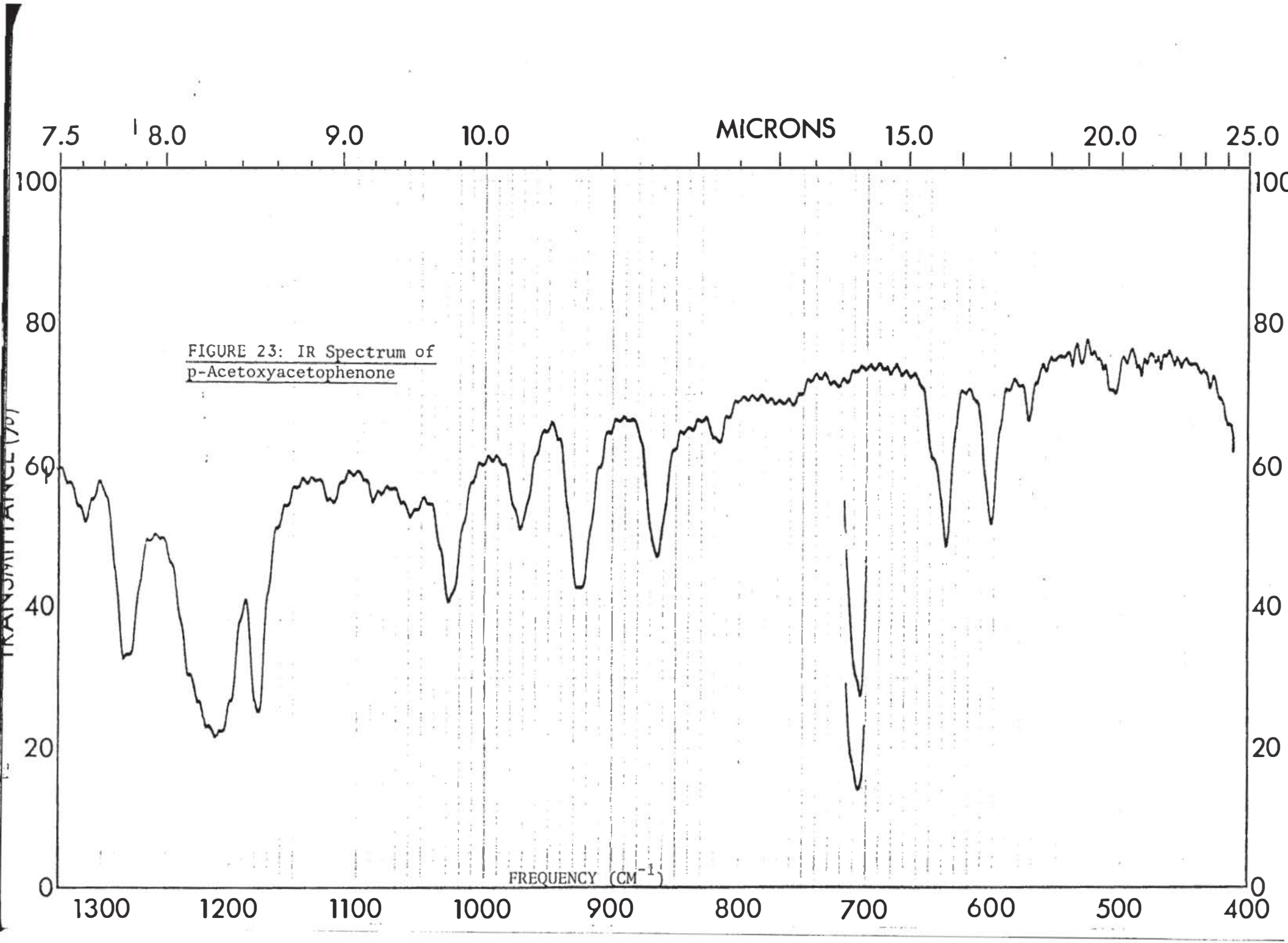


FIGURE 23: IR Spectrum of p-Acetoxyacetophenone

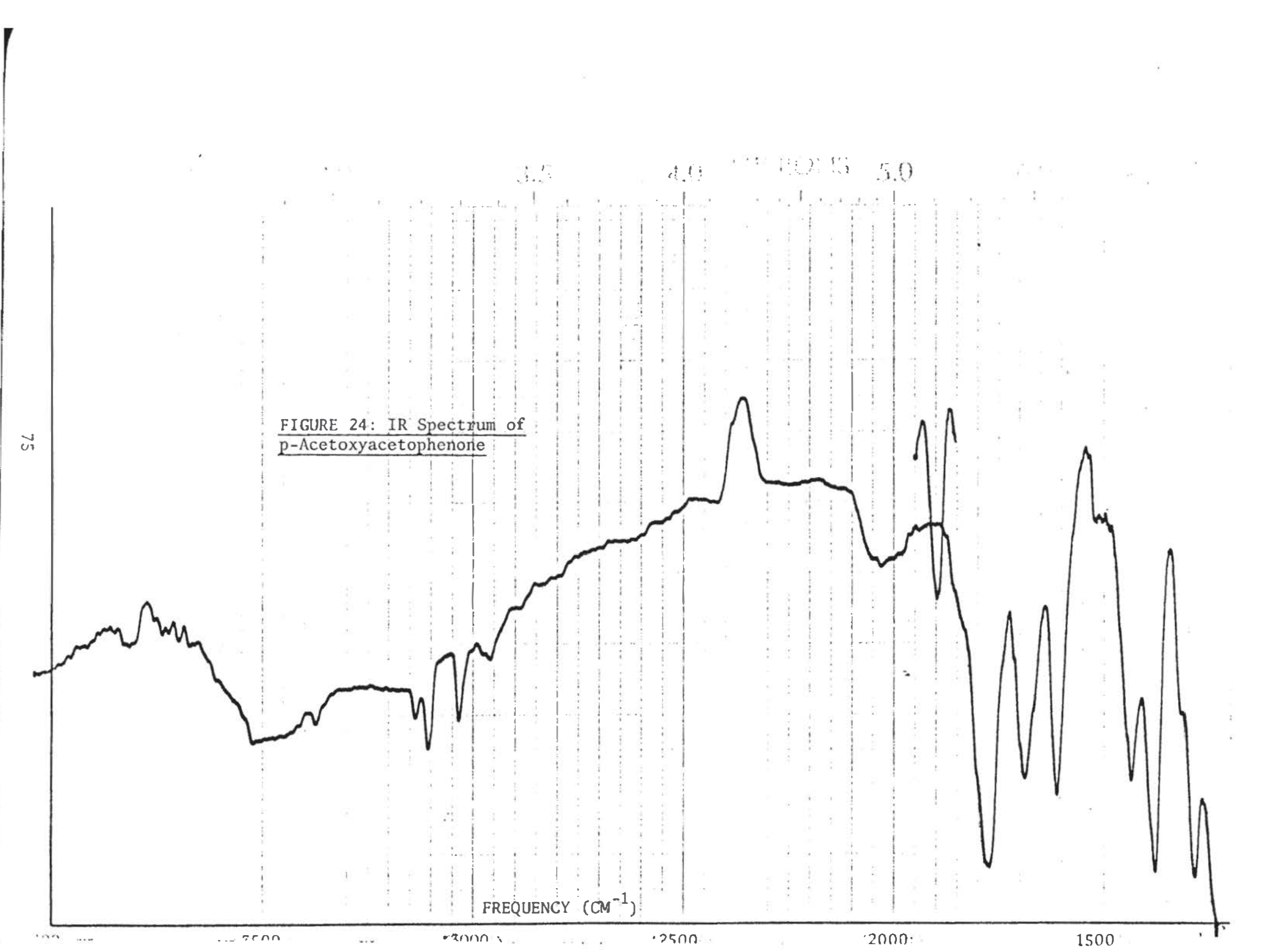


FIGURE 24: IR Spectrum of
p-Acetoxyacetophenone

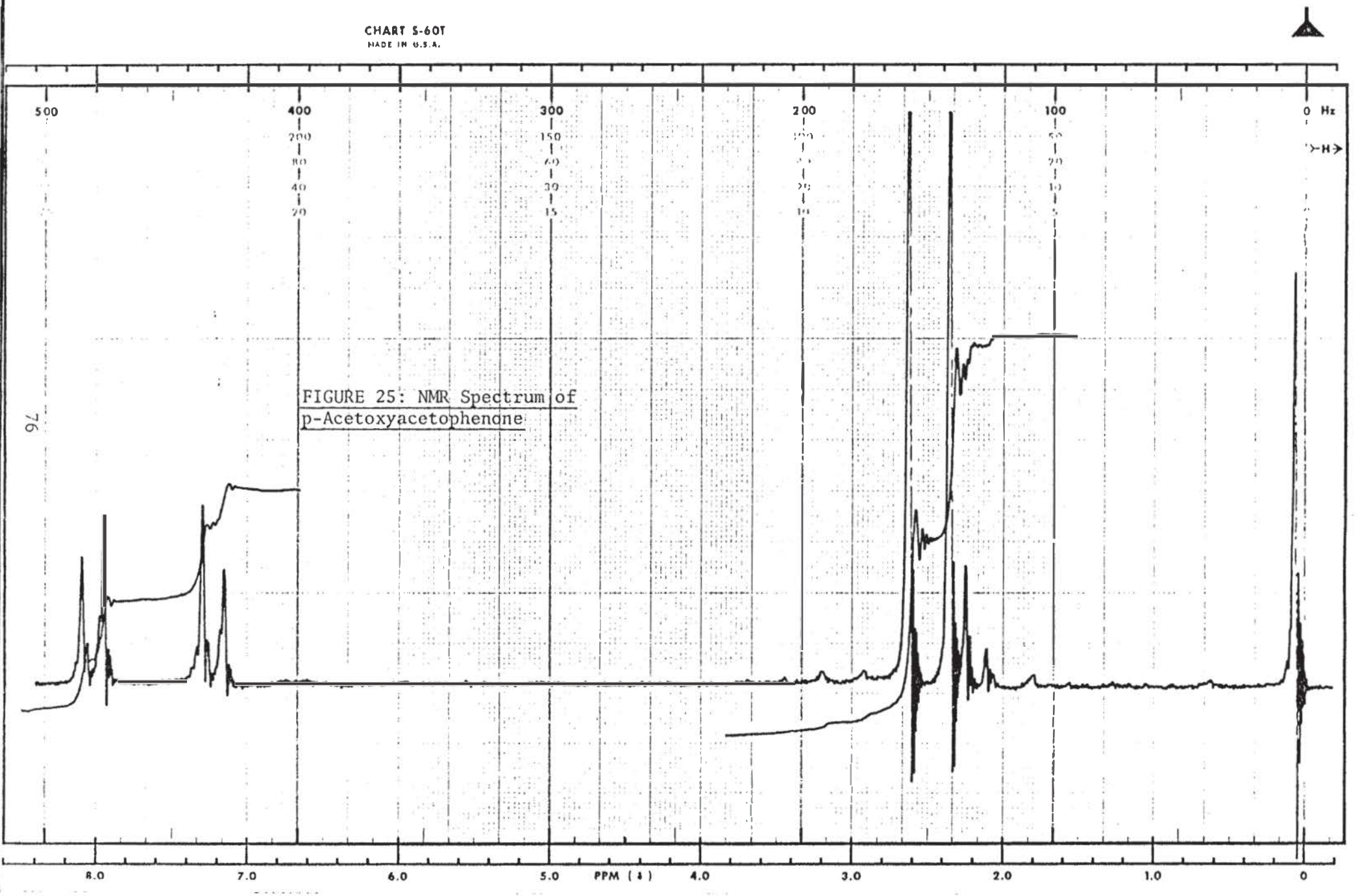


FIGURE 25: NMR Spectrum of p-Acetoxyacetophenone

RESULTS AND DISCUSSION

GC AND HPLC ANALYSIS.

All quantitative GC analyses were performed using the internal standard method. This method employs a calibration curve in which the abscissa is the ratio of the quantity of analyte, Q_i, to the quantity of standard, Q_s, and the ordinate is the corresponding ratio of the peak area of the analyte, A_i, to the peak area of the standard, A_s. Typically, 4 or 5 standard solutions were prepared. The data were analyzed by the method of least squares which gives the slope, m, and the Y axis intercept, b, of the line defined in equation 1. Using these two parameters derived from the standard solutions, the

$$A_i/A_s = m\ Q_i/Q_s + b \qquad (1)$$

known amount of internal standard added and the area ratios of the injected aliquot of the solution of interest, the amount of analyte was determined.

An effort was made to estimate the concentrations of the analytes in the reaction mixtures and to approximate those concentrations in the standard solutions. Similarly, care was taken to achieve relatively constant concentrations (varied enough that the area ratio of the solution under analysis was bracketed by the area ratios of the standard solutions) of internal standard in the standard solutions and the reaction solution. Detector non-

linearity due to concentration differences and injected volume variation was thus kept to a minimum[30] and the resulting curves were linear. New standard solutions were prepared for each analysis except where two similar analyses were run the same day.

As a rule, internal standards should be introduced early in sample processing. In the case of the ferric chloride/acetic anhydride ether cleavage reactions, the only potential internal standards with acceptable retention times were aromatic. The possibility of electrophilic substitution (see p. 85) demanded that the internal standard be introduced after the reaction mixture was quenched and extracted with diethyl ether. It is possible that a more thorough search would have produced an aliphatic inert compound with a suitable retention time.

Analyses by HPLC were performed in a manner similar to that with GC in that a least squares method was used on a sample containing an internal standard. A two-point calibration was used, each of the two standard solutions being injected and analyzed twice. Of necessity, all solutions were prepared in volumetric flasks. Two internal standards were often used to quantitate the analytes in a solution. This was done because of the widely differing detector reponses of the analytes.

In addition to the above method, the weight of the analyte was obtained directly from the data

processor/recorder when programed with the weight of the internal standard added. The program[31] calculated the slope, F1, and the y-intercept, F2, from equations 2 and 3 respectively.

$$F1 = \frac{C_1 \times C_s2 - C_2 \times C_s1}{C_s1 \times C_s2 \, (A_1/A_s - A_2/A_s)} \qquad (2)$$

$$F2 = C_2/C_s2 - F1 \times A_2/A_s2 \qquad (3)$$

Where: A_1 = peak area of standard sample 1

A_2 = peak area of standard sample 2

C_1 = concentration of standard sample 1

C_2 = concentration of standard sample 2

A_s1 = internal standard peak area of standard sample 1

A_s2 = internal standard peak area of standard sample 2

C_s1 = concentration of internal standard in sample 1

C_s2 = concentration of internal standard in sample 2

Using the slope and intercept determined by the above equations, the weight of the analyte was calculated from equation 4 and printed. Equation 4 is equivalent to

$$W_i = (F1 \times A_i/A_s + F2) \times W_s \qquad (4)$$

Where: W_i = weight of analyte

W_s = weight of internal standard

A_i = area of analyte peak

A_s = area of internal standard peak

equation 1 used in the work-up of GC data.

The use of only two points to define a linear standard curve in the HPLC analyses is justified in that an absorbance mode of detection was used. The use of GC thermal conductivity detectors is based on the observation that peak areas are roughly proportional to weight concentrations for a given compound. The absorbance detector is based on Beer's Law, which is linear for dilute solutions. Two points are used instead of one point and the origin because the design of some detectors does not demand a zero intercept.

SYNTHESIS OF MODEL COMPOUNDS

The synthesis of the model compounds and acyl-substituted model ethers in this study was accomplished by the Williamson method using lipophilic quaternary ammonium and phosphonium salts as phase transfer catalysts. The use of such catalysts is well documented.[32-37] The reaction to form unsymmetrical ethers generally proceeds with good to excellent yields. Only minor amounts of symmetric ethers are known to form even with a large excess of the alkyl halide (e.g. when used as solvent). The salts are readily available at low cost and are easily removed from reaction mixtures by washing with water.

The catalysts used were benzyltriphenylphosphonium

chloride, benzyltriethylammonium chloride and tetrabutylammonium bromide. The latter was used as the primary catalyst. It is purported to be particularly good for two-phase displacement reactions.[38] The benzyl triethylammonium cation is known to perform well for reactions involving hydroxide ion transfer and is useful in displacement reactions as long as the alkyl halide is highly active such as a benzyl halide. Benzyltriphenylphosphonium chloride proved to be a somewhat better catalyst for the phenyl phenethyl ether synthesis. The results of the syntheses involving phase transfer catalysis are shown in Table 13.

TABLE 13: Phase Transfer Syntheses

Ether	Catalyst	Reaction Conditions	Yield
Phenyl phenethyl	B	85°,18h	51.4%*
Phenyl phenethyl	C	85°,18h	42.8%*
Benzyl phenyl	A	25°,22h	101%**
p-Butoxyacetophenone	A	132°,19h	83.3%***
p-Benzyloxyacetophenone	A	25°,27h	95.3%**

*NMR Yield
**Isolated impure product
***Isolated pure product

A = Tetrabutylammonium bromide
B = Benzyltriphenylphosphonium chloride
C = Benzyltriethylammonium chloride

The synthesis of phenyl phenethyl ether was perfomed using phenethyl tosylate instead of halide. The possibility of an elimination reaction occuring upon the

reaction of the phenethyl substrate with base was the primary reason for choosing the tosylate. The phenethyl group has been well studied. Reactions of 2-phenethyl tosylates and bromides indicate that tosylates eliminate more slowly[39] (k_I/k_{OTs}=68 and k_{Br}/k_{OTs}=10) and that under conditions that usually lead to elimination, tosylates give good yields of substitution products.[40]

Phenyl 2-phenethyl ether was isolated in a yield of 38.7%. 2-Phenethyl bromide and the sodium salt of phenol react at 90° for 10 hours to give a 60% yield of phenyl 2-phenethyl ether.[41] The yield of p-butoxyacetophenone (the only other phase transfer synthesis in this thesis involving phenoxide attack on a non-benzyl carbon) indicates that the yield of phenyl phenethyl ether could be greatly improved by reaction at a higher temperature and/or with a better catalyst.

REACTIONS INVOLVING FERRIC CHLORIDE AND ACETIC ANHYDRIDE

The reaction of ferric chloride/acetic anhydride with coal model ethers was done to determine the usefulness of that method for 1) indication of coal structure, 2) reduction of molecular weight of a preasphaltene and 3) solubility increase of a preasphaltene. Benzyl phenyl ether was used as a test ether to optimize reaction conditions. The original method, as described by Ganem[22], consists of reaction of the ether with the reagents,

extraction with hexane, filtration, washing, drying, concentration and distillation. The substitution of diethyl ether for extractions in this thesis was the result of the possible need to extract phenol from the reaction mixture. Gas chromatography was used instead of distillation as a quicker and more quantitative method.

The typical reaction consisted of 1 - 1.5 grams of the ether, 0.5 grams of ferric chloride and 10 mL of acetic anhydride. The two attempted improvements on Ganem's work-up combined to give erroneous results. Ferric chloride is soluble in diethyl ether. During GC analysis, reactions of ferric chloride were suspected to be occurring in the injection port (170-250°) because of the nearly constant yield of phenyl acetate and benzyl acetate (see Table 14) and the absence of starting ether, despite the changes in reaction conditions. Neutraliza-

TABLE 14*: Initial Reaction Products of $FeCl_3$/ $C_4H_6O_3$ and Benzyl Phenyl Ether

Reaction Conditions	%Phenyl Acetate	%Benzyl Acetate
85°,3h	51.4	38.8
88°,22h	50.0	30.4
25°,3h	52.8	32.4

*The reactions for Table 14 are not included in the experimental section.

tion of the reaction mixture with sodium bicarbonate prior to extraction turned the fine black suspension of ferric chloride a red-brown color (presumably iron hydroxide). Results of the determinative reactions using the neutralization method are listed in Table 15.

TABLE 15: $FeCl_3/C_4H_6O_3$ Determinative Reactions with Benzyl Phenyl Ether

Reaction Conditions	%Phenyl Acetate	%Benzyl Acetate
25°,3h	6.1	8.4
80°,3h	29.4	22.6
80°,24h	44.0	27.8

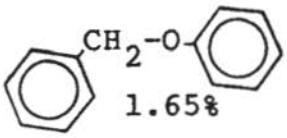
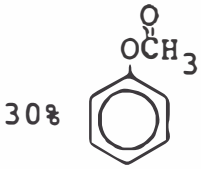
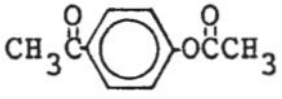
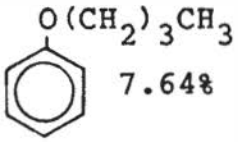
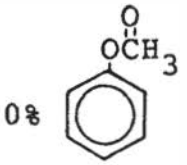
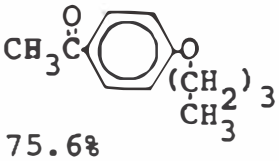
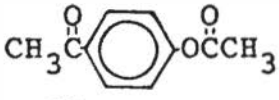
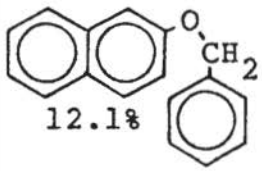
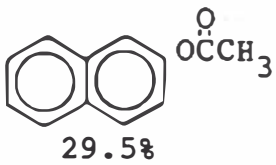
Since the same reactants would be used on a preasphaltene fraction of coal and the model ethers, it was desirable to use pyridine as solvent since the preasphaltene is completely soluble only in pyridine. Due to the basicity of pyridine it was suspected that no reaction would take place and, indeed, a reaction in pyridine produced only the starting benzyl phenyl ether. Acetonitrile was known to swell and be a partial solvent for Illinois Number 6 coals[42] and a reaction of benzyl phenyl ether in that solvent was performed. Due to the similar retention times of acetonitrile to phenyl acetate and benzyl acetate, the large preponderance of acetonitrile and the tailing of that solvent because of its polarity, no usable GC trace was obtained.

HPLC of ferric chloride/acetic anhydride ether cleavages in acetonitrile proved possible after some method development. The chromatographic technique described on page 32 was arrived at to exclude ferric chloride from the HPLC system. The fact that aromatic rings are acylated by Friedel-Crafts reactions was noted in the work of Ganem. In order to use the UV detector (254 nm), the internal standard necessarily had to be aromatic. The method consisted of addition of a pre-weighed internal

standard into a volumetric flask partially filled with the reaction mixture supernant. The supernant was used as a rinse and to fill the volumetric flask. Immediately after dissolution, one mL of the flask's contents was transferred by pipet to a syringe containing four mL of water for separation. By this method, the internal standard was in contact with the cool reaction mixture for approximately three minutes.

The results of the HPLC analyses are shown in Table 16. The yields of phenyl acetate from benzyl phenyl ether

TABLE 16: Reaction Products of $FeCl_3$/ $C_4H_6O_3$ and Model Ethers

Ether Recovery	Cleavage	Ring Substitution	Ring Subst. + Cleavage
 1.65%	 30%	 10.3%	 .0059%
 7.64%	 0%	 75.6%	 0%
 12.1%	 29.5%	----	----

and 2-naphthyl acetate from 2-naphthyl benzyl ether are almost identical, implying that the reactivity of the benzyl group is responsible for the amount of cleavage.

In contrast, Ganem found the results of benzylic ether cleavages largely dependent on the other half of the ether. He found "benzyl 2-octyl ether was converted to acetates (each 45%) faster than it underwent acylation but benzyl butyl ether was first acylated, then cleaved, to provide n-butyl acetate as the only hexane soluble product."[22] His explanation of the disappearance of benzyl acetate is not substantiated by the data in this work. The other ends of the model benzyl ethers (phenyl and 2-naphthyl) are more likely to undergo electrophilic substitution than the benzyl group but phenyl acetate and 2-naphthyl acetate were isolated. Ganem's work did not include analysis for acyl substituted starting ethers or acyl substituted cleavage products. Alternative explanations for the disappearance of benzyl acetate are offered beginning on page 95 of this thesis.

Since ferric chloride is a catalyst and acetic anhydride is present in 300% excess, one would expect cleavage after acylation of the ring, generating acetoxyacetophenone, which was not found in appreciable amounts. The ether is still present for cleavage and the ketone addition to the aromatic ring would retard further Friedel-Crafts substitutions. A possible explanation is found in Ganem's work. He found that addition of an equimolar amount of n-butyl acetate or 2-octyl acetate greatly retarded Friedel-Crafts acylation of benzyl acetate. He speculates that the ester carbonyl group is complexed to

ferric chloride and prevents acylation. For every ether cleavage two esters are generated. For every ring acylation, one acetate anion is left complexed to ferric chloride. The combined effect of these generated species is probably the reason for the observed phenomenon.

Acyl substitution could account for the low yields in the cleavage reactions. One would be forced to propose products not searched for, such as those resulting from non-para substitution, diacyl substitution, or acyl substitution of the benzyl ring as possible cleavage products. There is some evidence in the literature of anomalous orientations of Friedel-Crafts reactions. Saunders et. al.[43] found the orientation dependent on the amount of catalyst used. A 2:1 molar ratio of aluminum chloride to methyl 2-phenethyl sulfide (using acetyl chloride) gave a product that was 79% para-substituted while a 3:1 ratio gave almost entirely ortho-substituted product. Reaction of ethyl phenylacetate with aluminum chloride and acetyl chloride[44] gave equal amounts of para and meta isomers along with a small amount of ortho product. These results indicate the possibility of similar behavior in the ferric chloride catalyzed reactions. The molar ratio of ferric chloride to ether in this work was 1:3.

The results of the model ether cleavages showed that reaction of a coal fraction with ferric chloride/acetic anhydride would be largely dependent on the type of

ethers available for cleavage. In proposing to reduce the molecular weight of a preasphaltene, the competition between ether cleavage and ring substitution had to be considered. For a typical preasphaltene with a molecular weight of 1200, 28 acylations would negate the lowering of molecular weight by one ether cleavage. The ratio is even lower when it is considered that not every ether cleavage would result in the separation of the coal molecule into two parts.

Preasphaltene 282 was reacted with ferric chloride/acetic anhydride as detailed on pages 45 and 46. A simultaneous blank reaction was run identical to the former except that ferric chloride was omitted. The results of solubility studies performed on the reacted preasphaltene and the blank reaction are listed in Table 17. Table 18 contains the elemental analysis of preasphaltene 282 before and after reaction. Due to the insol-

TABLE 17*: Solubility Study of Ferric Chloride Reaction

	Pyridine	Toluene	Chloroform
Cleavage Reaction	I	I	I
Blank Reaction	S	I	11% S

*Solubility tests were run on the acetonitrile insoluble portion of the products. The cleavage reaction product was 94% insoluble and the blank reaction product 82% insoluble in acetonitrile.

TABLE 18: Elemental Analysis of Ferric Chloride Reaction

	%Ash	%C	%H	%N	%S	%O**	MW
Before Rxn	1.25	76.38	5.37	2.49	1.03	13.73	1247
After Rxn	1.44	69.62	4.93	1.94	1.03	21.04	----

**Oxygen was calculated by difference.

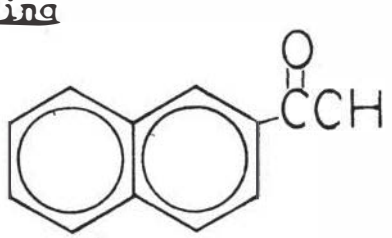
ubility of the product of the reaction, molecular weight determination was impossible by VPO. The oxygen content after reaction was calculated assuming that sulfur percentage did not change. The decrease in carbon, hydrogen and nitrogen content is undoubtedly due to the increase in oxygen. The H/C atomic ratios before and after reaction are .838 and .844. The corresponding N/C ratios are .0280 and .0239. The greater decrease in nitrogen is evidence that either nitrogen was lost in the reaction or that carbon and hydrogen were added but in a lesser proportion to oxygen than their proportion to oxygen in the original coal fraction.

The fact that the product of the reaction was essentially insoluble in pyridine indicates either a large increase in molecular weight or an alteration of the primary structure of the coal fraction. Acylation of phenolic groups almost certainly occurred. This would result in a partial loss of solubility as evidenced by the acetylation of preasphaltene 282 with acetic anhydride in pyridine and the resulting partial insolubility. However, saponification of the ferric chloride/acetic anhydride product did not increase solubility discernibly.

Evidence for electrophilic substitution on the preasphaltene was found in the IR spectra of several fractions. The ground coal was dried in an Abderhalden apparatus (100^{o},.2mm) both before and after making the

KBr pellet to exclude water from the spectra. Figure 27, page 91, is the spectrum of preasphaltene 282. Figure 28, page 92, is a spectrum of the preasphaltene after acetylation with pyridine and acetic anhydride. The ester carbonyl stretch at 1760-1720 cm^{-1} is slightly separated from the aromatic carbon stretch at 1630. The spectrum of the ferric chloride/ acetic anhydride reaction product in Figure 29 shows a new band at 1700-1680 cm^{-1}, presumably the aromatic methyl ketone carbonyl stretch. Figure 26 is representative of such a ketone. The 1760-1720 ester band

FIGURE 26: Model of Ring Acylation of Coal



is not evident in the latter coal spectrum, indicating little or no cleavage of ethers. The absence of this band is somewhat surprising (see ester carbonyl stretch in Figure 28) since phenol is acetylated quantitatively by ferric chloride/acetic anhydride. The phenolic groups in coal may be involved in intramolecular and intermolecular hydrogen bonding and therefore not present at the "surface" for reaction. Alternately, the aromatic carbons may react preferentially because of sheer abundance.

The possibility of ring acylation causing insolubility to the degree found in the ferric chloride/acetic anhydride reaction is remote. If the increase in percent

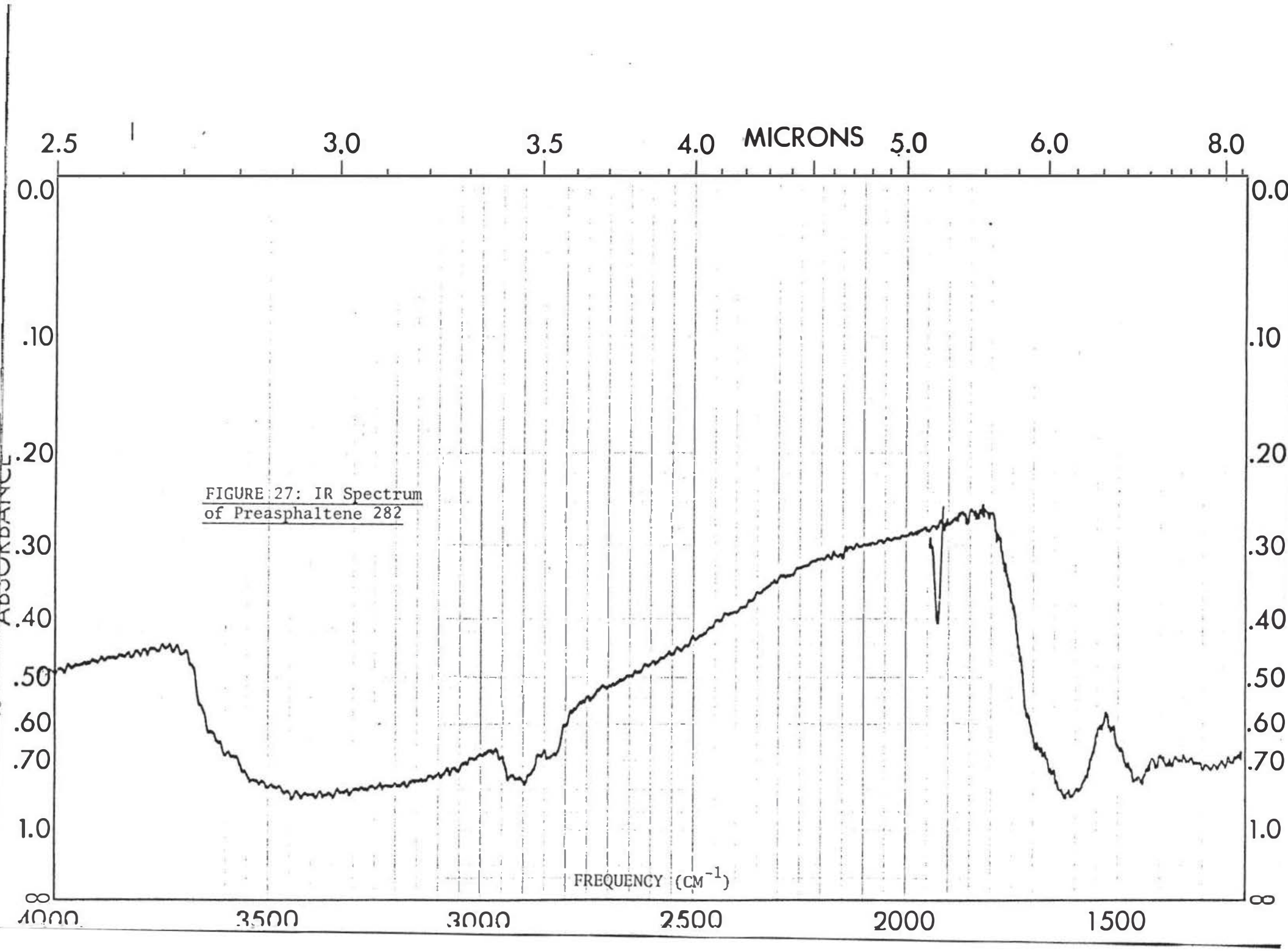


FIGURE 27: IR Spectrum of Preasphaltene 282

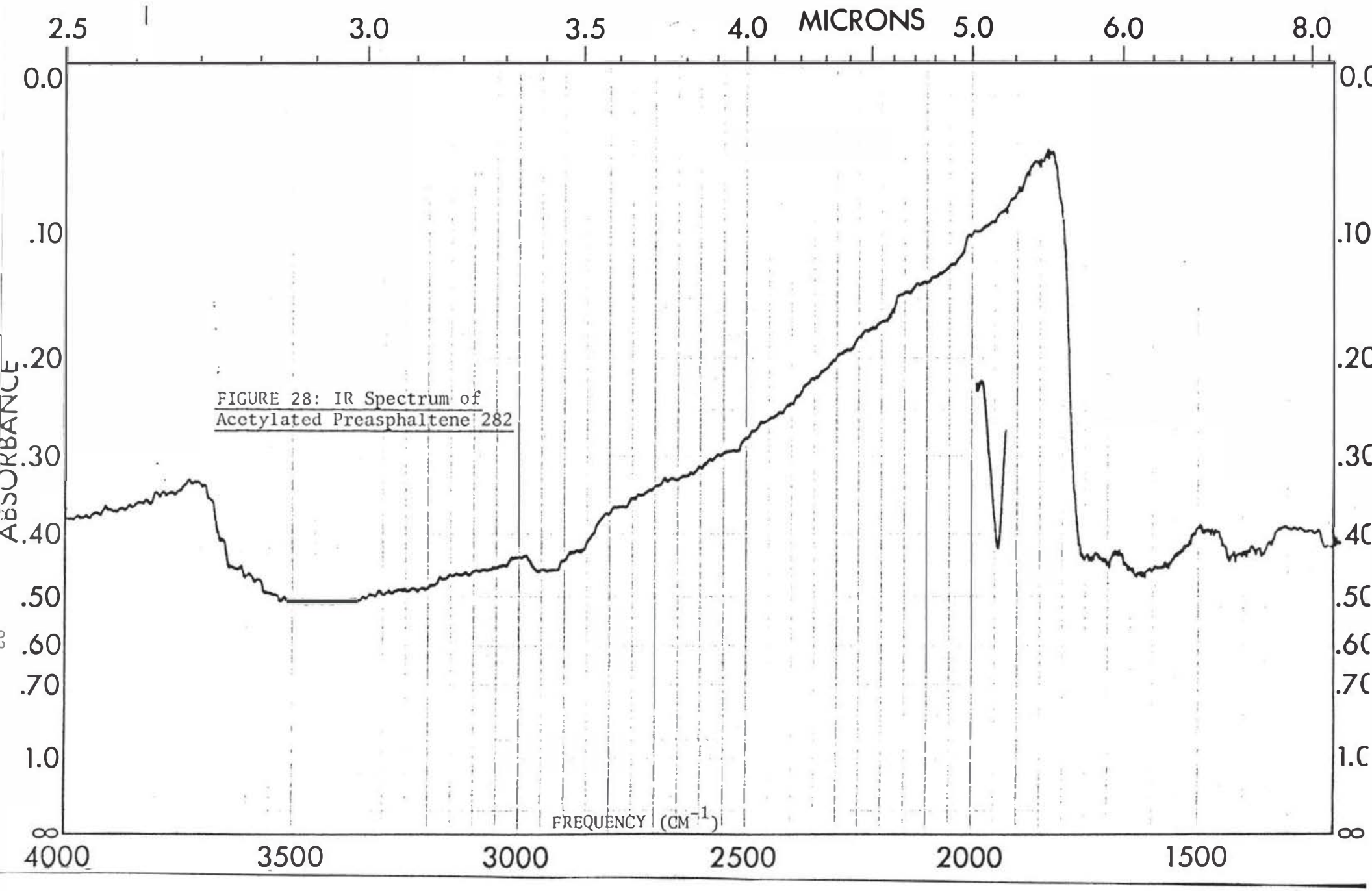


FIGURE 28: IR Spectrum of Acetylated Preasphaltene 282

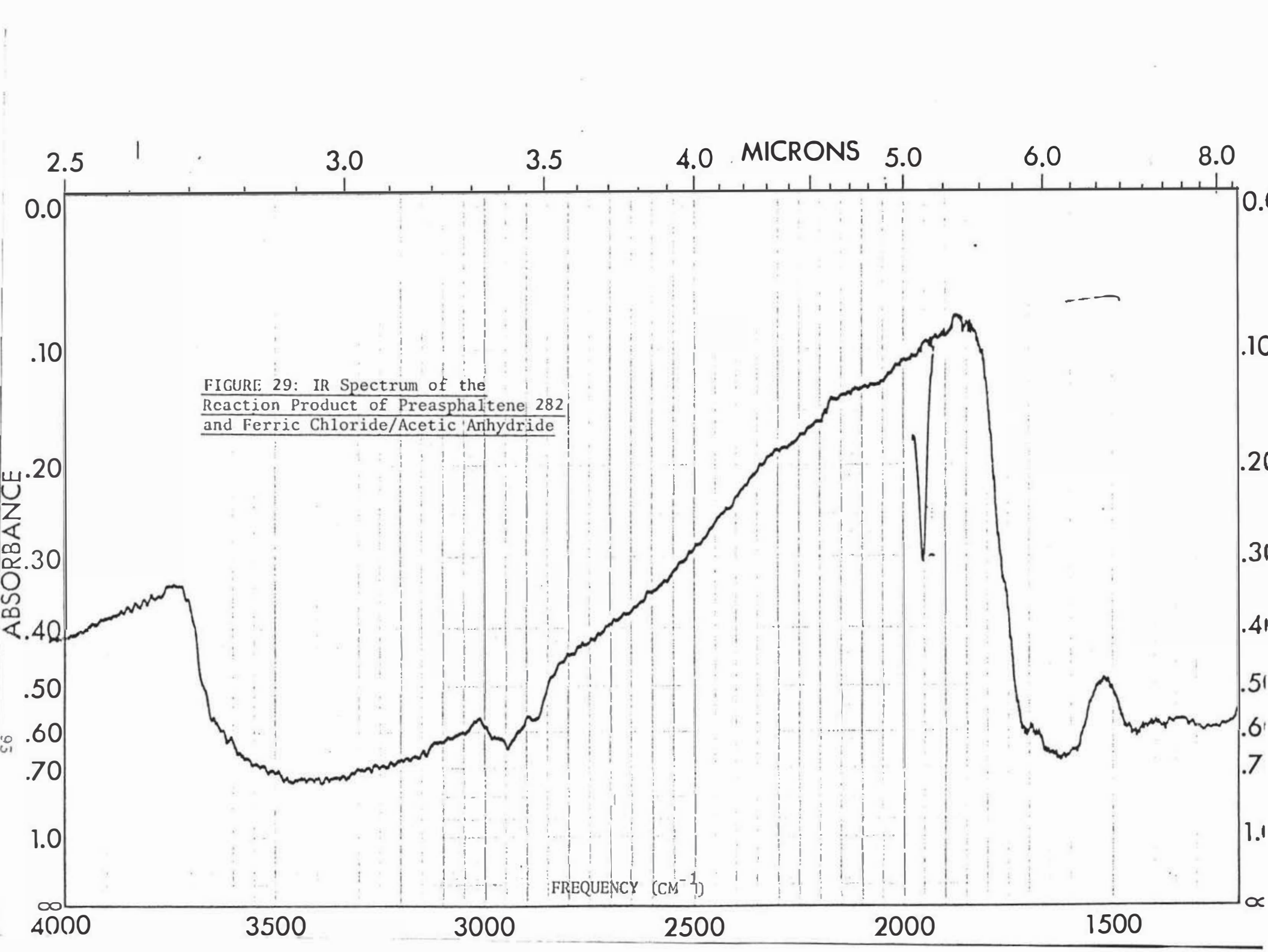


FIGURE 29: IR Spectrum of the Reaction Product of Preasphaltene 282 and Ferric Chloride/Acetic Anhydride

oxygen were entirely due to the formation of methyl ketones, the molecular weight would increase from 1247 to 1780 because of 12.7 electrophilic substitutions (see below) Molecular weight considerations aside, the ketones

MW of 282 preasphaltene = 1247; % O = 13.73.

$$\text{No. oxygen atoms/molecule} = \frac{(.1373)(1247)}{15.999} = 10.7.$$

Let x = # of acylations per molecule.
MW increase per acylation = 42.035.
% O in reacted preasphaltene = 21.04.
15.999 (10.7 + x) = .2104 (1247 + 42.035x)
x = 12.7

added should help solubilize the molecules in pyridine. The failure of a reacted preasphaltene to color a pyridine extract is too extraordinary to be accounted for by an increase of 43% in molecular weight.

The Friedel-Crafts acylations with aluminum chloride and aliphatic acyl chlorides at 46° as reported by Hodek and Kolling[45] increase the solubility of coals in pyridine even though the molecular weight is increased and the phenolic groups are acetylated. The extractability of the coals depends on the chain length of the inserted acyl group; acylation with acetyl chloride has little effect on the solubility of coals in pyridine. Four to five acylations per hundred carbon atoms were typical in that work. Using the worst case assumption made earlier that the increase in oxygen in the reacted preasphaltene 282 was due entirely to ring acylation, there occurred 16.4 acylations per hundred carbon atoms. That assumption

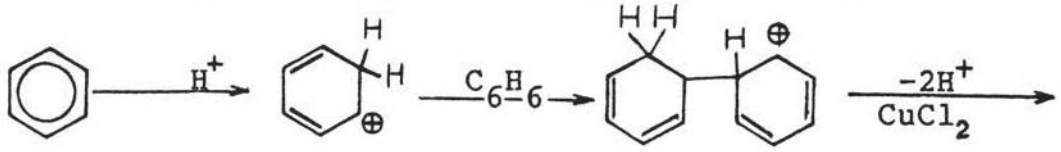
is obviously not supported by the findings of the above authors.

Hodek and Kolling[45] also found that respective reactions of a high volatile bituminous coal and a dry steam coal with anhydrous aluminum chloride in carbon disulfide at reflux gave products that were 50% less soluble and 400% more soluble in pyridine. They contend that Lewis acids can exert a cracking or a condensing effect. They further contend that the addition of an acyl chloride to the reaction scheme acts as a dispersive force between the molecules of coal by insertion of long side chains that reduce those effects. A criticism of their work is that they do not consider the cracking/condensing effect as significant despite their findings otherwise. A further criticism is that they do not consider the possibilty of ether cleavage and its effect on solubility.

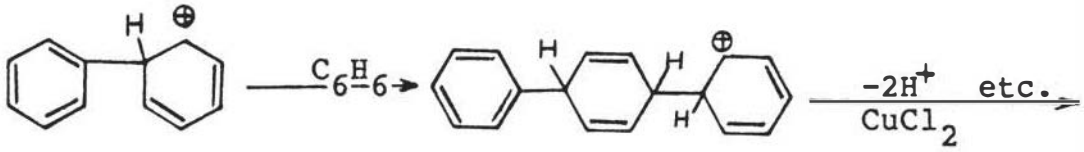
The reaction of Lewis acid metal halides with organic compounds is well studied.[46] Using relatively mild conditions (80^{o},8 min, N_2), isooctane has been reacted with anhydrous ferric chloride to give a product consisting of 81.4% isobutane.[47] Reactions with aromatic compounds (20 min.,80^{o}) give significant amounts of higher molecular weight compounds; usually the polymerized products are the result of side chain carbonium ion electrophilic attack on an aromatic ring.[48] Nuclear polymerization does result from the reaction of benzene (1 mole) with alumi-

num chloride (0.5 moles), 1 mL H_2O and cupric chloride (0.5 moles) at 37°, 30 minutes.[49] The authors suggest "oxidative cationic polymerization of aromatic nuclei" as

$$AlCl_3 + H_2O \longrightarrow H_2O \cdots\cdots AlCl_3 \longrightarrow H^+AlCl_3(OH)^- \quad (5)$$



(6)



(7)

a reaction sequence (equations 5-7) for the formation of polyphenyl. Deletion of either the Lewis acid or the oxidant from the reaction gives no solid product.

Polyphenyl is also prepared by Kovacic from benzene using ferric chloride.[50] The reaction is carried out using a 1:1 molar ratio of ferric chloride to water. The same reaction mechanism is proposed for equation 8, ferric chloride serving as both Lewis acid and oxidant. The

$$n\ C_6H_6 + 2n\ FeCl_3 \xrightarrow[70°,20\ min]{H_2O} \left[\bigcirc\right]_n + 2n\ FeCl_2 + 2n\ HCl \quad (8)$$

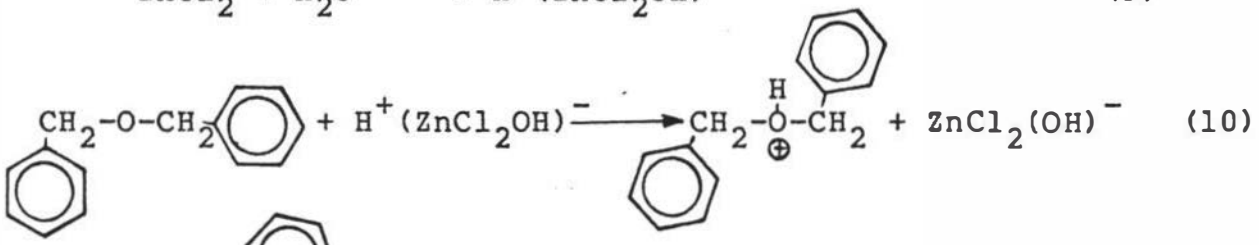
reaction of 1,4 cyclohexadiene with ferric chloride (40°) gave the dehydrogenation product, benzene, plus other products with longer GC retention times.

The presence of water in the above reaction is necessary to generate the Bronsted acid cocatalyst. Such an amount of water was not present in the coal or model

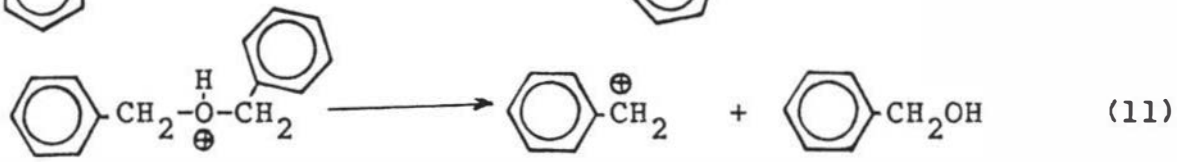
ether reactions of ferric chloride/acetic anhydride. The ferric chloride was kept in a vacuum desiccator but the presence of some water was likely considering the affinity and the number of openings of the desiccator. Given the increase in reaction time (6 days) and the fact that HCl is generated in the oxidation step of the above reaction, such a polymerization is not unlikely.

The reaction of coals with a hydrogen donor such as tetralin is accelerated by the use of zinc chloride.[51] The reaction of the model, dibenzyl ether, with zinc chloride with tetralin as solvent gives α and β isomers of benzyl-tetralin. When benzene is used, diphenylmethane is the product. Formation of the benzyl carbonium ion (Eq. 9-13) is responsible for the presence of the above reaction products. In the absence of an aromatic nucleus (when the solvent is cyclohexane) tars form (Eq. 14)

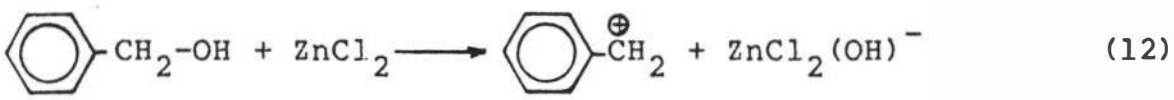
$$ZnCl_2 + H_2O \longrightarrow H^+(ZnCl_2OH)^- \qquad (9)$$



(10)



(11)



(12)

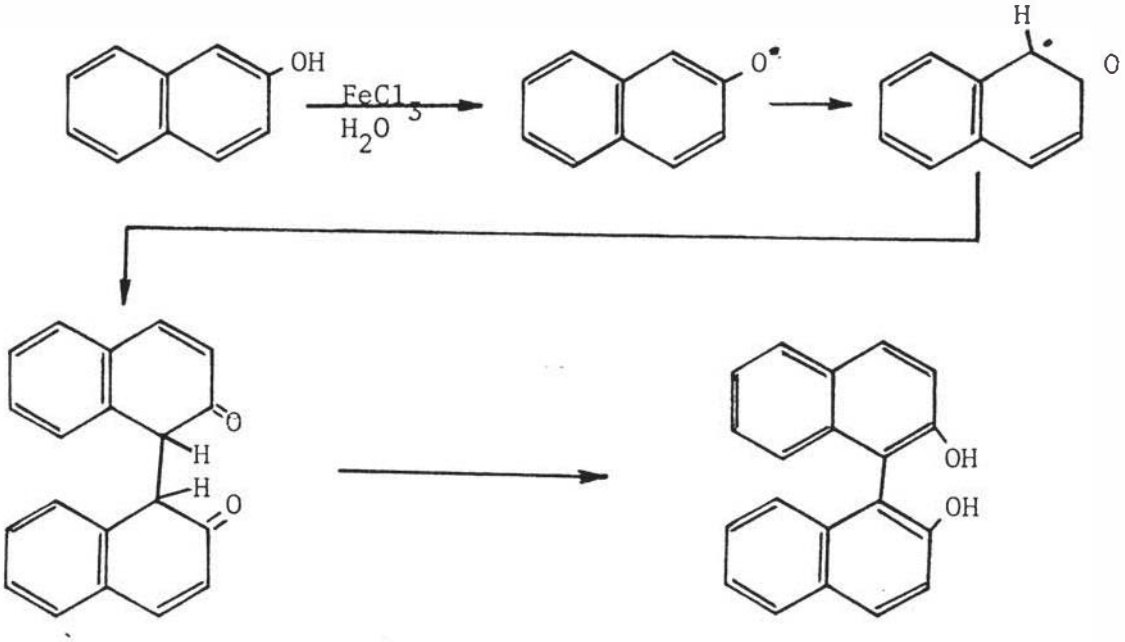
(13)

(14)

and no lower lower molecular weight materials are observed. This is analagous to what possibly happened in the reaction of preasphaltene 282 with ferric chloride and acetic anhydride. There the only aromatic ring available for electrophilic substitution was the coal fraction itself. Two crosslinks could result from the cleavage of one dibenzyl ether type crosslink. Benzyl phenyl ether or benzyl naphthyl ether undergo asymmetric cleavage to give phenol and naphthol respectively plus the benzylium ion addition product; no increase in crosslinks would be generated in coal were these the type of ether bridges present. These zinc chloride cleavages are carried out at 325° for 1 hour - conditions far more rigorous than those employed in the cleavage reactions in this study. In the latter case, the benzylium ion would be less available to react with the coal because of the presence of the acetate anion generated from acetic anhydride. However, relatively few intermolecular crosslinks would be necessary to cause insolubility in the preasphaltene.

The consistently lower yields of benzyl acetate as compared to phenyl acetate in the cleavage of benzyl phenyl ether is supporting evidence for the above proposed reaction scheme. No benzyl acetate was found when the solvent used in the cleavage reactions was acetonitrile. Benzyl acetate was a product when excess acetic anhydride was used as solvent. This adds credence to Ganem's statement that ferric chloride is complexed to carbonyl moieties and its effects are moderated by that complexation.

The well known oxidative coupling reaction of phenols is another hypothetical cause of the insolubility of the ferric chloride/acetic anhydride reacted preasphaltene. Reaction 15 shows the oxidation of 2-naphthol by aqueous ferric chloride to di-β-naphthol.[52] The phenoxyl radical



(15)

is resonance stabilized by a radical with the unpaired electron on a carbon positioned ortho to the oxygen atom. Dimer-

ization of the latter structure, followed by enolization, regenerates the phenolic groups, which can react further.

There is no exact accounting of the fate of the reacted preasphaltene 282. The structure is a complex unknown. The reagents used can react in a variety of ways. All of the reactions described above could be taking place: ether cleavage resulting in lower molecular weights, ring acylation, cleavage of alkyl linkages, ether cleavages resulting in further crosslinking and crosslinking by aromatic nucleus condensation. It is interesting to note that the work of Hodek and Kolling[45] is very similar - using anhydrous aluminum chloride and acyl chlorides for one hour reactions of coal. Although their reaction using acetyl chloride was not successful in increasing solubility, neither did they find a significant decrease in solubility. Reduction of the reaction time (6 days) of the ferric chloride/ acetic anhydride system is clearly indicated should further work be done. This reaction would be applicable to coal reactions in an empirical way (i.e. changing reaction times and temperatures, varying the reactant ratios, and changing solvents). Given the numerous reactions possible, it would be impossible to ascribe the results to any one reaction. It has, therefore, little value as an indicator of structure but could be a method of solubilizing coals for further work. It may have less value in that regard than

other Lewis acids (e.g. aluminum chloride) because of its oxidizing properties.

ACETYLATION WITH PYRIDINE AND ACETIC ANHYDRIDE

The determination of phenols with pyridine in acetic anhydride as performed by van Krevelan et. al.[11] is a method that leaves room for unconscious manipulation by the subjective researcher. It is not the method that should ultimately be the standard in coal analyses but is among those methods that are currently used.

The procedure consists of acetylation of the phenols, saponification of the acetate ester, acidification, distillation of the acetic acid and titration with standard base. The overall reactions are shown in eq. 16-18.

$$\text{COAL-OH} + \begin{matrix}\text{CH}_3\text{-C=O}\\ \\ \text{CH}_3\text{-C=O}\end{matrix}\!\!>\!\text{O} \xrightarrow{\text{py},90^\circ} \text{CH}_3\text{-COOH} + \text{COAL-OOCCH}_3 \quad (16)$$

$$\text{COAL-OOCCH}_3 + 1/2\ \text{Ba(OH)}_2 \xrightarrow{100^\circ} \text{COAL-OH} + 1/2\ \text{Ba(OOCCH}_3)_2 \quad (17)$$

$$1/2\ \text{Ba(OOCCH}_3)_2 + 1/3\ \text{H}_3\text{PO}_4 \longrightarrow \text{CH}_3\text{COOH} + 1/6\ \text{Ba}_3\text{(PO}_4)_2 \quad (18)$$

Distillations and titrations are continued until "the amount of acid in the distillate is constant." The amount of acid in the last titration is then subtracted from each previous titration. The remaining acid is used to calculate the amount of phenolic material in the sample as in Eq. 19. In fact, the amount of acid was seldom

$$\text{mmol phenol } g^{-1} = (v_1 + v_2 + v_3 + ...v_n - nv_{n+1})\ (t/a) \quad (19)$$

where: t = molarity of NaOH
a = grams of sample
v = mL of NaOH in each titration

constant but diminished with every distillation. The stopping point was open to interpretation. This author made it standard practice to stop after ten distillations for the preasphaltene 252 phenol determinations. This was too arbitrary a method since the amount of acetic acid in each distillation seemed dependent on the amount of water present in the distillation flask at the initiation of the distillation. The initial amounts of water were difficult to standardize due to the opaque layer formed on the inside of the distillation flask after several runs. The amount of acid may also have been dependent on the rate of distillation. The rate of distillation was not standardized in this work. Phenol determinations on preasphaltenes 282 and C-22440 and their reaction products were stopped when there was an obvious repetition of the amount of titrant. Failing that, the process was stopped when the amount of titrant was below one mL and gradually declining. At 20 cycles of distillation and titration, the experiment was stopped regardless of titrant volume. There was no observable reason for the differing behavior of the various coal fractions.

The acidic distillation material responsible for the background varied from .014 to .056 milli-equivalents for

the last 40 mL distillation. What the background consisted of chemically has not been determined. Low molecular weight phenols have been proposed. Were that the case, the amount of these phenols distilling over would not be a constant but would be reduced with each subsequent distillation just as the amount of acetic acid is. Thus, the method would give high results for the amount of phenolic material present.

The only direct comparison of results of phenol determinations with other methods comes from the laboratory of Leon Stock at the University of Chicago.[53] Quantitative NMR studies on isotopically methylated preasphaltene C-22440 gave 3.5 to 4.0 phenols per 100 carbon atoms. Results by the van Krevelan method (see Table 19, page 111) gave 6.7 phenols per 100 carbon atoms. Yarzab et. al.[54] found that bituminous coals contain approximately one phenolic group per 20 carbon atoms. They plotted percent oxygen as phenols vs. percent carbon on various coals and determined a line by least squares fit that is described by Eq. 20. Preasphaltene C-22440 con-

$$\%OH = 33.2 - 0.35\ \%C \qquad (20)$$

tains 78.92 percent carbon on a dry, ash-free basis. Using that number as an approximation of the dry, mineral matter-free carbon content and equation 20 the coal fraction should contain 5.58 percent oxygen as phenols. This transforms to 3.49 mmoL of phenol per gram or 5.24 phenolic groups per 100 carbon atoms. Since preasphaltenes

are lower in percent carbon and higher in percent oxygen than their precursor coals and since the solubility of preasphaltenes depends on the pyridine-phenolic group relationship, the number of phenols per 100 carbon atoms should be higher than 5.24. This is supporting evidence that the acetylation method figure is preferable to the one determined by Stock's group. The methylation procedure has not been critically evaluated by the scientific community and, until such time, the acetylation results will be considered approximately correct.

There are several critcisms of the acetylation method of counting phenols. The acetylation reaction is not homogeneous since the coal fraction is not completely soluble in the 1:2 acetic anhydride: pyridine solvent. It is insoluble in the saponification step where the reaction medium is water. That the acetylated preasphaltenes could not be regenerated to a completely soluble product by saponification was evidence that the saponification step is not as efficient as the acetylation step or, alternately, that other reactions occur during the saponification step. Infrared analysis of hydrolyzed acetylated coals[10] show the time required for hydrolyzation to be more than that prescribed by van Krevelan.

Other functional groups besides phenols could be acetylated. Primary and secondary amines would react and be hydrolyzed slowly but there is no evidence for the

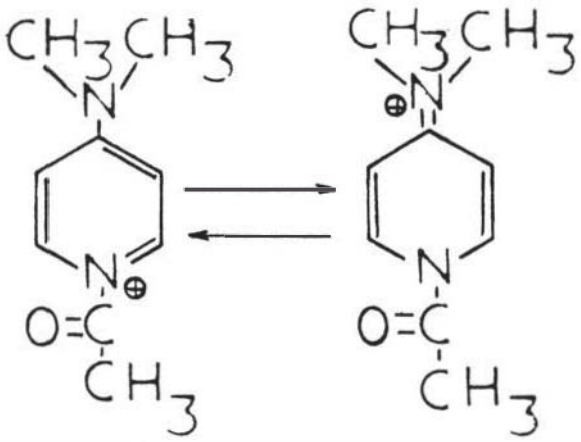
presence of these groups in coal. This author is not aware of any systematic study of nitrogen functional groups in coal. It is believed that part of the ammonia released during the pyrolysis of coals is produced from amines.[55] Thiols, if present, would also be acetylated. Preasphaltene C-22440 contained 1.08% sulfur compared to 12.08% oxygen while 282 analog had 1.03% to 13.48%.

The van Krevelan phenol determination method is one that requires no expensive spectroscopic equipment. It is familiar to all coal researchers and has withstood the test of time. If the results are not accurate, they are at least approximate and are reproducible. Comparison between laboratories is possible but further standardization is necessary to define a stopping point (number of titrations or amount of titer per titration). There is evidence that results are dependent on mesh size[56]; perhaps this should be standardized also but a mesh size requirement could not be easily applied to preasphaltenes.

The use of the above standard procedure was modified by the use of p-dimethylaminopyridine (DMAP) as catalyst in the acylation step. As previously stated, this was done to ensure the reaction of hindered phenols. The 4-amino substituent adds to the basicity of pyridine. Pyridine has a pK_a of 5.21 while DMAP has a pK_a of 9.71.[57] The powerful catalytic effect is not a reflection of the basicity alone however. The pK_a of triethylamine is 10.7 but no such effect is seen with its use. The stability of

an acylpyridine intesmediate (Figure 30) is thought to be the reason for the catalysis.

FIGURE 30: Acylpyridine Intermediate



As a check of the method of phenol measurement in coals, two of the coal model ethers were reacted with acetic anhydride in pyridine. As expected, no cleavage or electrophilic substitution occured with either benzyl phenyl ether or phenyl phenethyl ether. Impure benzyl phenyl ether was recovered (114%) and no other products were present by GC. Phenyl phenethyl ether was recovered in a 99.5% GC yield.

OXIDATION OF PREASPHALTENES

As is often the case in research, matters not originally intended for study assume an importance that demands attention. Two seemingly anomalous results will be discussed in this section: 1) the inability to achieve a pyridine soluble fraction of the Illinois No. 5 coal

sample (Penn State 252), and 2) the decline with time of the phenolic content of the preasphaltenes studied.

The fact that no pyridine soluble fraction of the 252 coal could be isolated was undoubtedly due to oxidation during workup. The vacuum on the Abderhalden apparatus was inadvertently broken while the fraction was drying at 100°. Efforts to redissolve the coal fraction in pyridine thereafter showed partial insolubility. Although care was taken and and several attempts made to re-extract, re-precipitate the filtrate with toluene and recover the fraction, in each case the product was not pyridine soluble after drying.

The oxidation of bituminous coals has been studied in a variety of ways. Ignasiak et. al.[58,59], using labeled oxygen, oxidized a bituminous coal prior to pyrolysis. The detection of $C^{18}O_2$, $C^{18}O^{16}O$ and a high concentration of ^{18}O in the tar and water fraction suggested to them that condensation reactions between hydroxyl groups led to ether crosslinks and the production of labeled water. This result naturally implies that the initial oxidation products include phenolic or aliphatic hydroxyl groups. They used coal dilation and fluidity as a measure of crosslinking. The reduction in the two parameters is not due to all the oxygen taken up but only to a fraction that is capable of condensation reactions.

Wachowska et. al.[60] similarly found that mild oxida-

tion (85°, 4 days) partially destroyed the swelling properties of a bituminous coal. They used the ether cleaving method of potassium in tetrahydrofuran on the coal and the oxidized coal, resulting in the lowering of the softening point and a large increase in dilation. The values of these properties after cleavage were essentially the same for fresh and oxidized coal. These results were attributed to the formation of ether crosslinks from the condensation of hydroxyl groups.

Infrared Fourier transform studies by Pearson et. al.[61] on a coal along an exploration adit indicate an increasing carbonyl group formation, with increasing crosslinking as measured by swelling indices and other parameters, as the seam nears the end of the adit. The spectrum of the least exposed coal is used as a standard and subtracted from the other spectra to measure the oxidation effects. Shoulder peaks at 1585, 1650 and 1690 cm^{-1} are reported as carboxylate anion, highly conjugated and singly conjugated carbonyl groups respectively. A weak shoulder at 1765 cm^{-1} is ascribed to a phenyl ester. Their hypothesis is that ester crosslinks are formed by initial oxidation products such as carboxyl groups condensing with already existing hydroxyl groups in the coal. Wachowska's regeneration of swelling properties on reaction of oxidized coals with potassium in THF was cited as evidence of cleavage of those ester linkages.

There are several criticisms of Pearson's work:

1.) The method of subtracting the spectrum of a sample from the middle of the adit from the spectra of the more oxidized coal using the kaolinite bands at 1035 and 1010 cm^{-1} as standards is admitted to be subjective. It also assumes a constant kaolinite concentration throughout the coal seam.

2.) Wachowska could detect no increase in carboxyl groups in an oxidized bituminous coal by an ion exchange method.

3.) The work of Morterra and Dow[62] rules out the assignment of 1600 cm^{-1} bands on oxidized carbon materials to carbonyl-like species. The assignment of that band to an aromatic C=C vibration is stressed although the importance of the presence of oxygen on the carbon is noted. "It is thought that it is indeed the existence of an oxidized layer mainly formed by ether-like bonds crosslinking the aromatic chains which gives the polyaromatic network enough asymmetry, i.e. dipole moment change with vibration, to make what is basically a C=C mode IR active at 1600 cm^{-1}." The shoulder peak at 1585 cm^{-1} could be ascribed to such an enhancement by oxidation of an undetermined sort. The 1650 and 1690 cm^{-1} shoulder peaks could be overtone and combination bands increased through oxidation. The fact that these bands exist in the spectrum of the coal in the middle of the coal seam (although to a lesser degree) leads one to believe that

they are the result of an oxygen functionality present in fresh coal. Carbonyl groups are thought not to be present in bituminous coals with the possible exception of quinones.

4.) Should the 1650 and 1690 cm^{-1} bands result from ketone carbonyl stretch, as Pearson himself states "it is difficult to conceive of a mechanism by which the ... formation of ketones.....leads to the covalent cross-linking responsible for the loss in swelling characteristics and other caking properties." The formation of methyl ketones from Friedel-Crafts acylation of preasphaltene 282 with ferric chloride and acetic anhydride gave a peak at 1690 cm^{-1} (see page 92) of much greater intensity than that observed in the difference spectra of Pearson.

The above discussion involves two scenarios for coal oxidation and no clear answer is yet at hand. The case for ether crosslink formation is less accompanied by marginal data but is proven to no greater degree. Pearson finds no evidence for ether formation in oxidized coals. Liotta[63] finds the only substantial difference between weathered and fresh coals in the infrared is the ether group content. Whichever crosslink theory is correct (both may be), the effect is the same in either case. Both require the formation of an oxidized species - a phenol in the ether case, an acid in the ester case - that reacts further at a later time to produce a cross-

link. It would seem that drying a coal fraction would increase the liklihood of crosslink formation as, in each case, water is a product of the condensation. Wachowska reports the swelling properties of an oxidized coal that has undergone cleavage are reduced by heat treatment under vacuum. This is analagous to the behaviour of the 252 preasphaltene, which became insoluble after drying under vacuum. The present evidence points to a condensation reaction and resultant molecular weight increase as reasons for the insolubility observed.

The phenolic content of the preasphaltenes isolated are shown in Table 19. A time period of one week elapsed

TABLE 19: Phenolic Content of Preasphaltenes (mmol/g)

Preasphaltene	1st Det'm	2nd Det'm	3rd Det'm
252	5.15	4.28	3.40
282	5.33	4.82	4.20
C-22440	4.47	4.42	----

between the preasphaltene 252 determinations. The second analysis of preasphaltene 282 was done a day after the first and the third a week later. The two analyses for the C-22440 fraction were performed simultaneously. A definite decline with time of the number of phenolic groups counted can be seen. That the phenols reacted in some manner seems certain. The logical assumption is that they reacted with air. The preasphaltenes were kept in a vacuum desiccator common with coal and other dry, solvent free coal fractions. No record was kept of the number of times the desiccator was opened.

The decline with time of the phenolic content of the preasphaltenes cannot be easily explained by an ether crosslink mechanism. The formation of additional phenols is required for that occurence. More than half the added phenols would have to react with preexisting phenols for an overall decrease to take place. This likelihood is remote. The phenomenon is best explained by the ester formation theory of Pearson. Addition of acid groups that would react with the phenols present would explain the data. Regardless of the reason, a trend was seen in the data that has not been reported heretofore in the measurement of phenols in coal fractions.

Two phenol determinations of smaller than 120 mesh 252 coal were done ten days apart. The values obtained were 4.31 and 4.29 mmoL of phenol per gram. The analysis done by Penn State before the coal arrived at this university gave 4.30 mmoL of phenol per gram.[64] The phenolic content did not change despite the sieving of the coal in air. The process of oxidation occured much more readily in the preasphaltenes. Given the mild conditions responsible [1) opening the vacuum desiccator to the atmosphere or 2) reaction with dissolved oxygen during the pyridine extraction] for oxidation in the case of the 282 preasphaltene, the reaction should be a matter of concern for coal researchers using that general fraction for study.

PYRIDINE HYDRIODIDE REACTIONS WITH PREASPHALTENES

Mayo et. al.[17,65] report a decrease in molecular weight, an increase in phenolic content and incorporation of iodine on reaction of preasphaltenes derived from Illinois No. 6 coals with hydrogen iodide in pyridine and other solvents. The data are consistent with cleavage of ether crosslinks in the coal fractions. In an effort to substantiate the cleavage of ethers by pyridine hydriodide in pyridine (a more convenient system than use of HI), Sy and Buchanan[65] used that reagent on model compounds. Negative results on simple ethers were intriguing and gave the indication that knowledge of cause of reaction in preasphaltenes might lead to a better understanding of coal structure.

Larsen's work[4], described earlier, indicates that all hydroxyl groups in coal are proximate to an ether oxygen. Genthner's infrared analysis[66] of deuterium exchanged Illinois No. 6 coals indicates that the phenols are hydrogen bonded. Sy and Buchanan report cleavage of o-anisic acid with pyridine hydriodide to give salicylic acid. No cleavage is observed with p-anisic acid, leading to their conclusion that hydrogen bonding may be responsible for cleavages of ethers in coal by pyridine hydriodide. A structure such as that in Figure 5, page 14, is proposed as representative of coal ethers.

In an effort to evaluate the above hypothesis, the phenols in preasphaltenes 282 and C-22440 were acetylated, to remove possible hydrogen bonding, prior to reaction with pyridine hydriodide. The reaction products are compared with those of unacetylated coal fractions in Table 20. The increase in phenolic groups is consistent with cleavage but no significant reduction in molecular weight is observed. The fact that the analyses for the two reactions are so similar all but precludes any anomalous behavior due to technique. The only variation from Mayo's experimental method was in the washing of the

TABLE 20: Analyses of Preasphaltenes and Reacted Preasphaltenes

	282	PyHI+ 282	PyHI+ Acet. 282	22440	PyHI+ 22440	PyHI+ Acet. 22440
MW	1247	1119	----	1322	1222	----
PHENOL*	4.78	7.16	5.88	4.44	7.06	5.31
% ASH	1.25	----	----	0.88	----	----
% C	76.38	76.14	73.75	78.23	72.54	----
% H	5.37	4.96	4.98	5.50	5.26	----
% N	2.49	2.24	2.55	2.23	2.03	----
% S	1.03	----	----	1.08	----	----
% I	----	2.01	1.17	----	6.06	----

*mmol g^{-1}

reaction products. Instead of rinsing the product with hydrochloric acid and water in the filter funnel, the 282

and C-22440 reacted fractions were stirred overnight with 10% HCl under nitrogen prior to filtration and water washing. The analyscs of reaction products by Mayo are repeated from Figure 3 in Table 21. All the reactions are

TABLE 21

	WATER	TOLUENE	PYRIDINE
*MW	901	275	373
% I	4.0	37.5	23.4

*The MW of the original preasphaltene is 1283.

performed with hydrogen iodide; the solvents vary. The same preasphaltene is used in each case.

Analysis by VPO gives a number average molecular weight as defined by the formula in Equation 21. The pro-

$$MW_N = \frac{\sum N_i m_i}{\sum N_i} \quad (21)$$

ducts of each molecular mass m_i and the number of molecules N_i having that mass are added and that total is divided by the total number of molecules. Number average molecular weights are disproportionately influenced by the lower molecular weight materials. Billingham[68] uses the example of a 1% by weight impurity of molar mass 100 g mol^{-1} in a polymer with a molar mass of 10,000 g moL^{-1}. The molecular weight by VPO of the impure polymer would be 5050, despite the fact that over 99% of the mass was due to the heavier molecules.

It is possible that all the iodine determined by elemental analysis in Mayo's reacted preasphaltenes is

present as iodide salt formed when the nitrogen atoms present in the preasphaltenes became protonated. Hypothetically, when the iodide incorporated preasphaltene was dissolved in pyridine for molecular weight determination, the protonated nitrogen atom would lose its proton due to the overwhelming proportion of pyridine nitrogens available for protonation. One molecule of pyridine hydriodide would be generated (and counted as a molecule by the VPO) in the solution for every iodide ion present. Table 22 contains molecular weights (of a preasphaltene incorporated with iodine as HI of original molecular weight 1283) calculated as a function of percent iodine. It also contains molecular weights calculated from the assumption that all the iodine present in Mayo's preasphaltenes is in the form of pyridine hydriodide. Sample calculations of each hypothetical situation are shown below. The

TABLE 22: Molecular Weights Calculated From Percent Iodine Incorporation

%Iodine INCORPORATED	MW IF AS HI	MW IF AS PyHI
5	909	901
20	512	476
30	408	362
45	322	266

Let x = number of iodide ions added as HI per molecule of preasphaltene in a 5% iodide incorporation.

$$\frac{127\ x}{1283 + 128x} = .05 \ ; \ x = .532$$

$$MW_N = \frac{53.2(207) + 100(1283)}{153.2} = 909$$

Let x = number of iodide ions added as PyHI per molecule of preasphaltene in a 5% iodide incorporation.

$$\frac{127\ x}{1283 + 207x} = .05\ ;\ x = .550$$

$$MW_N = \frac{55(207) + 100(1283)}{155} = 901$$

calculations assume that pyridine hydriodide exists in pyridine as non-solvated ion pairs.

Washing with hydrochloric acid could lead to ion exchange with the hypothetical preasphaltene-iodide salt, generating the corresponding chloride salt. Using the 282 pyridine hydriodide reaction as an example (page 46), 0.4205 g of the preasphaltene (2.5% nitrogen) contains 7.51×10^{-4} moles of nitrogen. The reaction product was washed with 400 mL of 10% HCl (approximately 20 moles of water). The competition for the hydrogen halides between the nitrogen atoms in the preasphaltene and the water molecules favors the latter over the former (2.7×10^4:1 molar ratio). Statistically, some chloride salts would be present but further studies would be necessary to determine the expected amount. The iodine remaining in the washed preasphaltene is not unexpected. The salts were formed in a homogeneous reaction. Water washing of the hydrophobic coal fraction would not be a totally efficient means of removal.

Hypothesis of iodine incorporation as pyridine hydriodide needs no accounting for chloride exchange during washing. Both salts would be removed (to the

extent that water would reach the incorporated pyridine salt).

Figure 31 is a graph of molecular weight as a function of incorporated iodine as determined in Table 22. The solid line represents retention of iodine as a iodide salt formed with a protonated preasphaltene nitrogen atom. The broken line represents iodine present in the preasphaltene as pyridine hydriodide. The triangular points come from Mayo's data in Table 21. The latter are within experimental error of one and sometimes both theoretically derived lines. Molecular weights of preasphaltenes are somewhat inaccurate due to the fact that benzil is used as a calibrant. Billingham[67] states that vapor pressure osmometry can be considered reliable only if it is calibrated with standards having molecular masses in the same range as the sample. This observation, combined with the evidence in Figure 31 and the data obtained in this work, casts some doubt about the ability of pyridine hydriodide to cleave ethers in coal fractions.

It should be recorded that other preasphaltene reactions by Mayo using pyridine hydriodide in pyridine give molecular weights that do not closely match calculations from percent iodine. Table 23 lists those reaction products. The molecular weight determinations there and in Table 21 were performed by several workers. This fact is noted because of the extreme difficulty in achieving

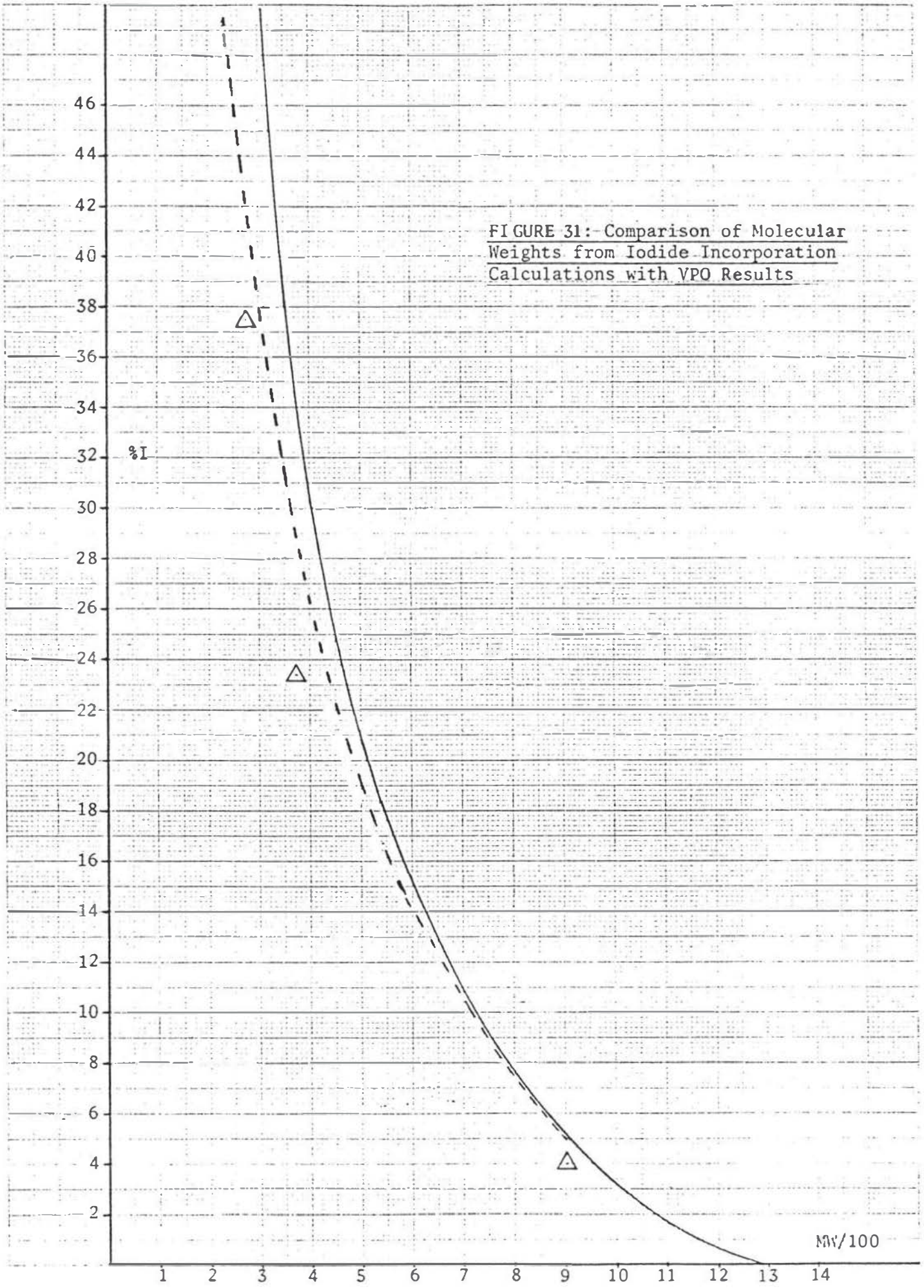


FIGURE 31: Comparison of Molecular Weights from Iodide Incorporation Calculations with VPO Results

TABLE 23: Molecular Weights Calculated From Iodine Incorporation

MW of Initial Fraction	%I	Theoretical MW As HI	Theoretical MW As PyHI	VPO MW
1250	9.15	730	714	462
790	3.39	685	683	548
1090	5.15	842	803	430

meaningful data from VPO when dealing with preasphaltenes. This author's research group has been unable to determine molecular weights matching those obtained from Galbraith Laboratories despite successful determinations of organic compounds. The values obtained by experiment are somewhat greater than one-half those purchased. This author feels molecular weights should be performed by an experienced technician, dedicated exclusively to that purpose. Should the theory of iodide incorporation be correct, the differences in VPO molecular weights from the thoretically calculated ones may be only an indication of how accurately the analyses were performed.

The nitrogen content of the pyridine hydriodide reacted preasphaltenes is a limit on the amount of iodide that can be incorporated as hydrogen iodide or as the pyridine salt. The only reaction by Mayo that does not have an atomic nitrogen surplus is the reaction of hydrogen iodide in toluene (see Table 21, page 115). Mayo reports 1.4% nitrogen and 30.0% iodine. The nitrogen/iodine molar ratio for this product is 1/2.3, exceeding the one to one limit imposed by the iodine incorporation theories. However, Mayo describes the solvent in that

reaction as being red from molecular iodine. Thus the excess iodine in the reacted preasphaltene could be due to addition to double bonds or to substitution on aryl side chains. Mayo's reaction of a preasphaltene (MW = 1090) with molecular iodine in pyridine gave a product with 34.1% iodine, 1.96% nitrogen and an apparent molecular weight of 602. There is therefore some ambiguity in the interpretation of the point in Figure 31, page 119, derived from the reaction of pyridine hydriodide in toluene.

Calculations similar to those shown previously were performed on preasphaltenes 282 and C-22440 and are listed in Table 24. The percent iodine in the reacted C-22440

TABLE 24: Molecular Weights Calculated From Iodine Incorporation

	282	22440
% I	2.01	6.06
MW OF PREASPHALTENE	1247	1322
CALC. MW IF HI ADD'N	1073	875
CALC. MW IF PYHI ADD'N	1070	862
MW AFTER PYHI RXN	1119	1222

preasphaltene would seem to indicate greater cleavage than in the reacted 282 fraction but this is not borne out by the molecular weight decrease. Since any of the above iodine incorporation schemes (including ether cleavage) decrease the observed molecular weight, a logical assumption is that either the percent iodine or the

molecular weight determination is incorrect.

The phenolic content of the the preasphaltenes in creased after reaction and this is evidence in favor of cleavage of ethers. The fact that there is no attendant molecular weight change can be attributed theoretically to cleavage of intramolecular crosslinks. Alternatively, the previous discussion of oxidation may have some relevance. If ethers were formed from oxidation products either prior to or after reaction with pyridine hydriodide, any ether cleavage would be partially negated. It should be noted that molecular weights in this work are the result of analyses performed by Galbraith Laboratories. The procedure entails days of mail time and possible air oxidation.

An obvious explanation of the differences in the results obtained in this work and Mayo's data is that the coals that are precursers to the preasphaltenes are not the same in their starting materials and geological histories. They therefore give different results on reaction with pyridine hydriodide. This reconciliatory interpretation is certainly valid but it is not conducive to further elucidation of the problem. The possibility of basic structural differences in the coals is acknowledged, but further work is needed to prove that the molecular weight reductions as seen by Mayo are not artifacts of the method used.

The phenolic content of the pyridine hydriodide

reacted preasphaltenes in Table 20, page 114, would initially seem to give credence to the hydrogen bond theory of Larsen.[23] However, since the data in Table 20 are calculated on a per gram basis, the phenolic content of the acetylated preasphaltenes must be adjusted to account for the increase in weight due to acetylation. The corrected values are 7.06 and 6.32 mmoL of phenol per gram for the reaction products of the acetylated 282 preasphaltene and the corresponding C-22440 fraction respectively. A sample calculation of these data is shown below. These values do

$$\frac{4.78 \text{ mmoL phenol}}{\text{g } 282} \times \frac{1247 \text{ g } 282}{\text{moL } 282} = \frac{5.96 \text{ moL phenol}}{\text{moL } 282}$$

$$\frac{42 \text{ g moL}^{-1}}{\text{Acetylation}} \times \frac{5.96 \text{ Acetylations}}{\text{Molecule}} = \frac{250 \text{ g moL}^{-1}}{\text{Molecule}} = \text{MW Increase}$$

$$5.88 \times \frac{1247 + 250}{1247} = \frac{7.06 \text{ mmol phenol}}{\text{g starting material}}$$

not differ significantly from the values for the non-acetylated reaction products.

Field ionization mass spectrometry (FIMS) is an ideal method for characterization of polymers with a range of molecular weights. The mass spectrum envelope produced is a good representation of the molecular weight distribution of the sample since no fragmentation occurs in the ionization chamber. Ionization occurs on application of a high potential gradient to the sample. This force is sufficient to remove an electron, generating only parent ions.[69]

Figures 32-35 are spectra of C-22440 preasphaltene derivatives produced by FIMS.[70] Figure 32 is the spectrum of the preasphaltene, Figure 33 of that fraction reacted with pyridine hydriodide, Figure 34 of the acetylated preasphaltene and Figure 35 is the spectrum of the acetylated preasphaltene after reaction with pyridine hydriodide. Table 25 contains the data extracted from the mass spectra. The molecular weight of the pyridine hydriodide

TABLE 25: FIMS Characterization of Preasphaltene C-22440 and Reaction Products

Sample	MW_N	MW_M	% Volatile
1	504	552	34
2	388	442	31
3	220	261	10
4	196	230	10

Sample 1 = Preasphaltene C-22440
Sample 2 = Preasphaltene reacted with PyHI
Sample 3 = Acetylated preasphaltene
Sample 4 = Acetylated preasphaltene reacted with PyHI

reacted preasphaltene was lower than that of the original preasphaltene. However, since the samples were not completely volatilized, no molecular weight reduction by pyridine hydriodide can be inferred.

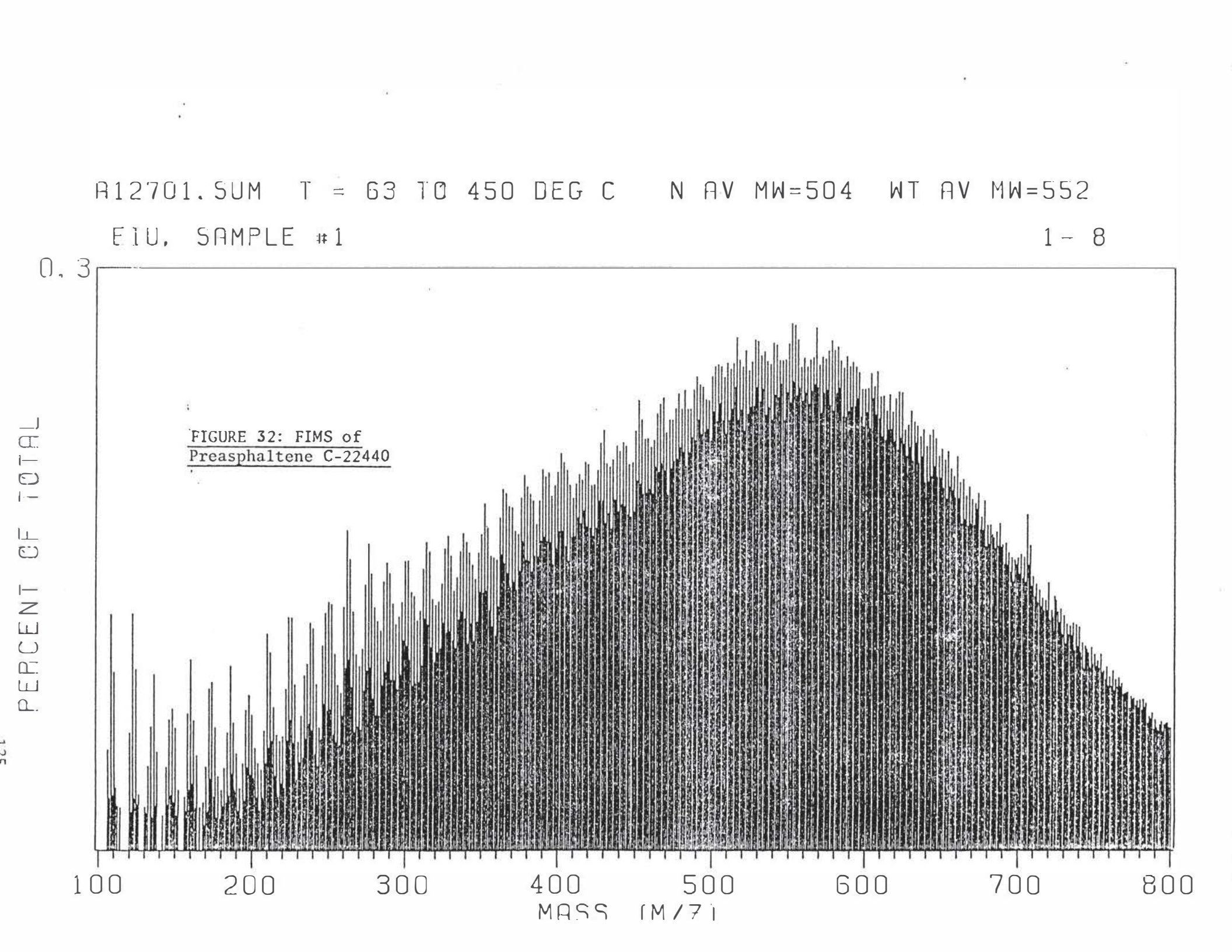


FIGURE 32: FIMS of Preasphaltene C-22440

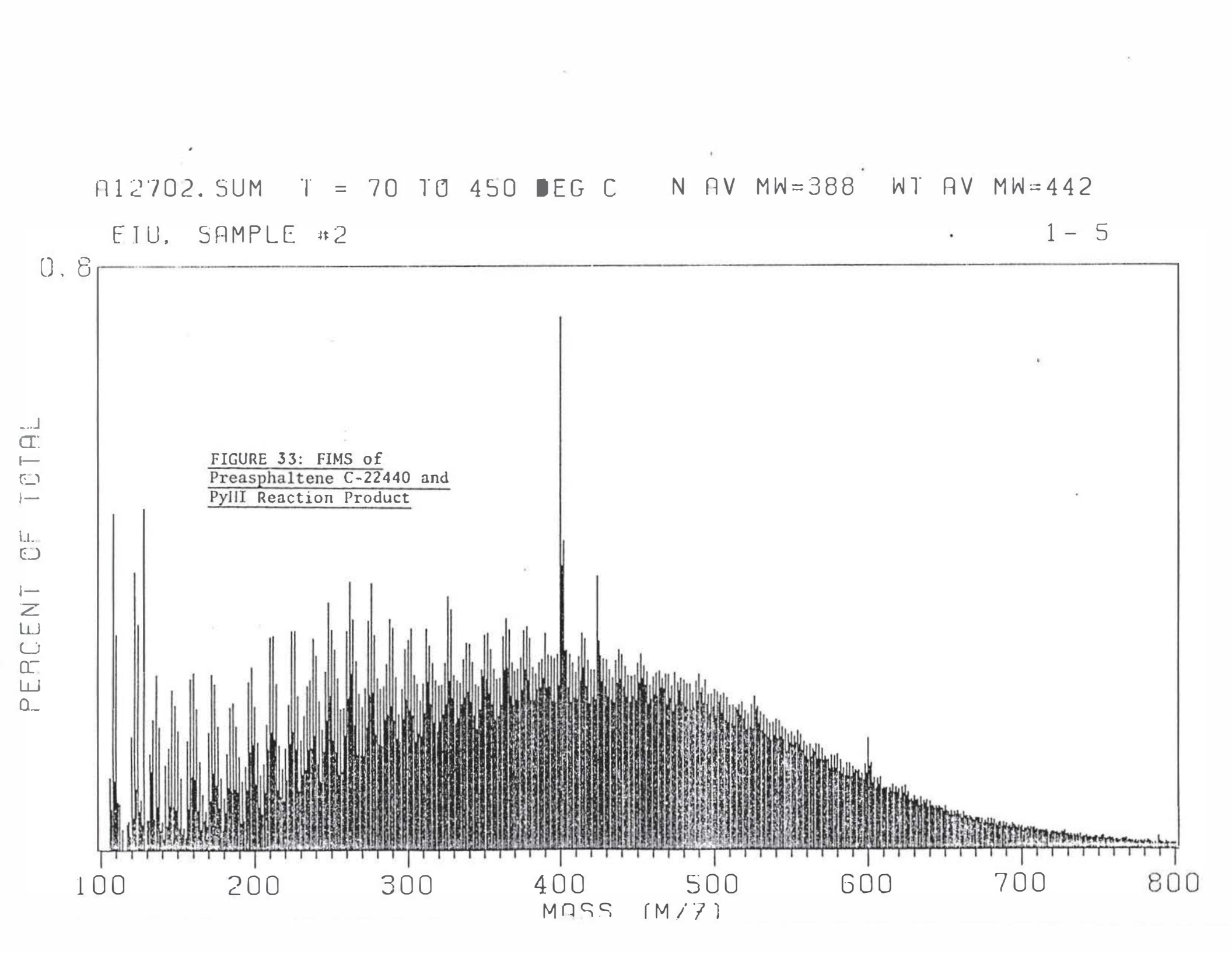


FIGURE 33: FIMS of Preasphaltene C-22440 and PyIII Reaction Product

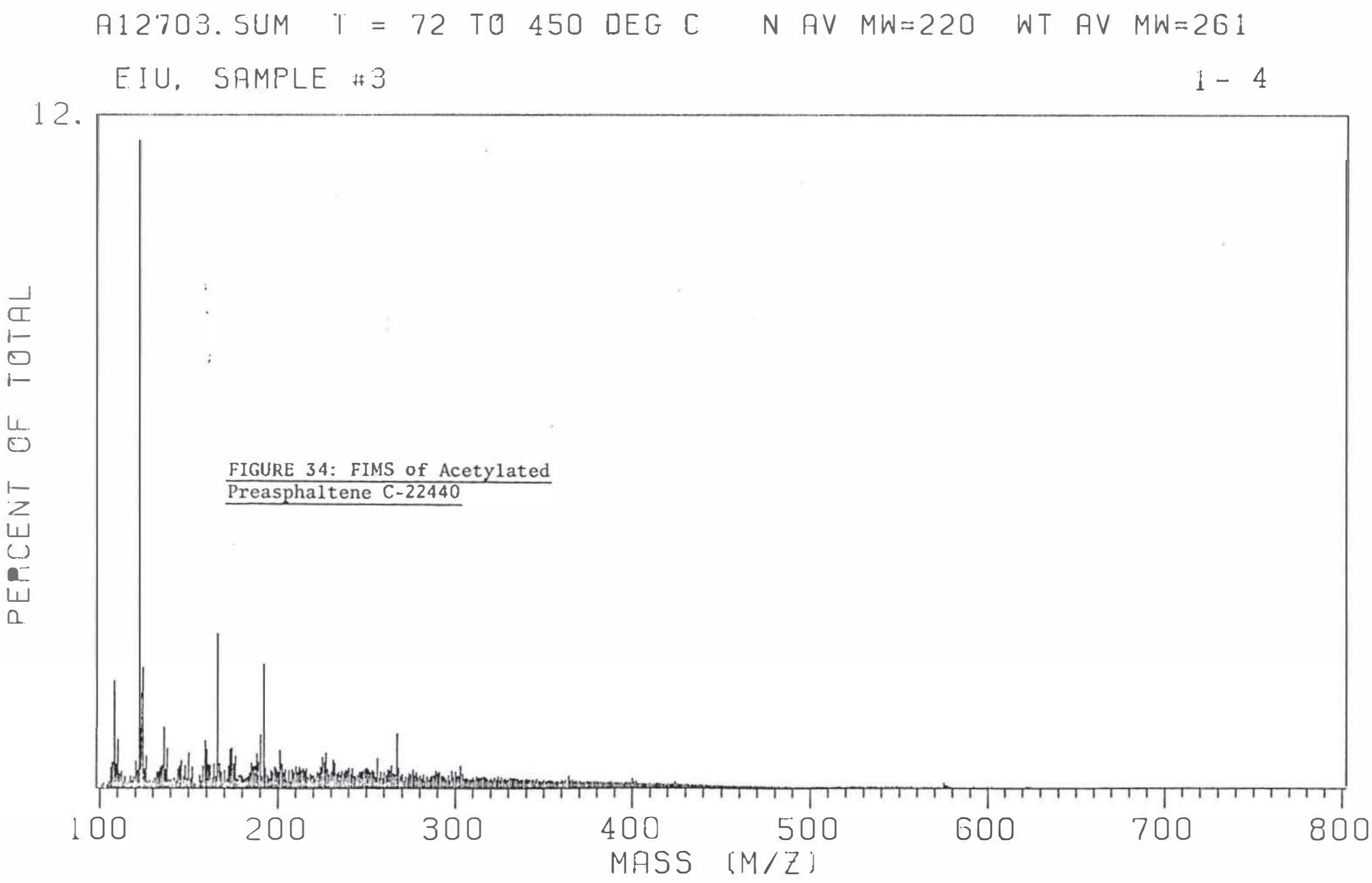


FIGURE 34: FIMS of Acetylated Preasphaltene C-22440

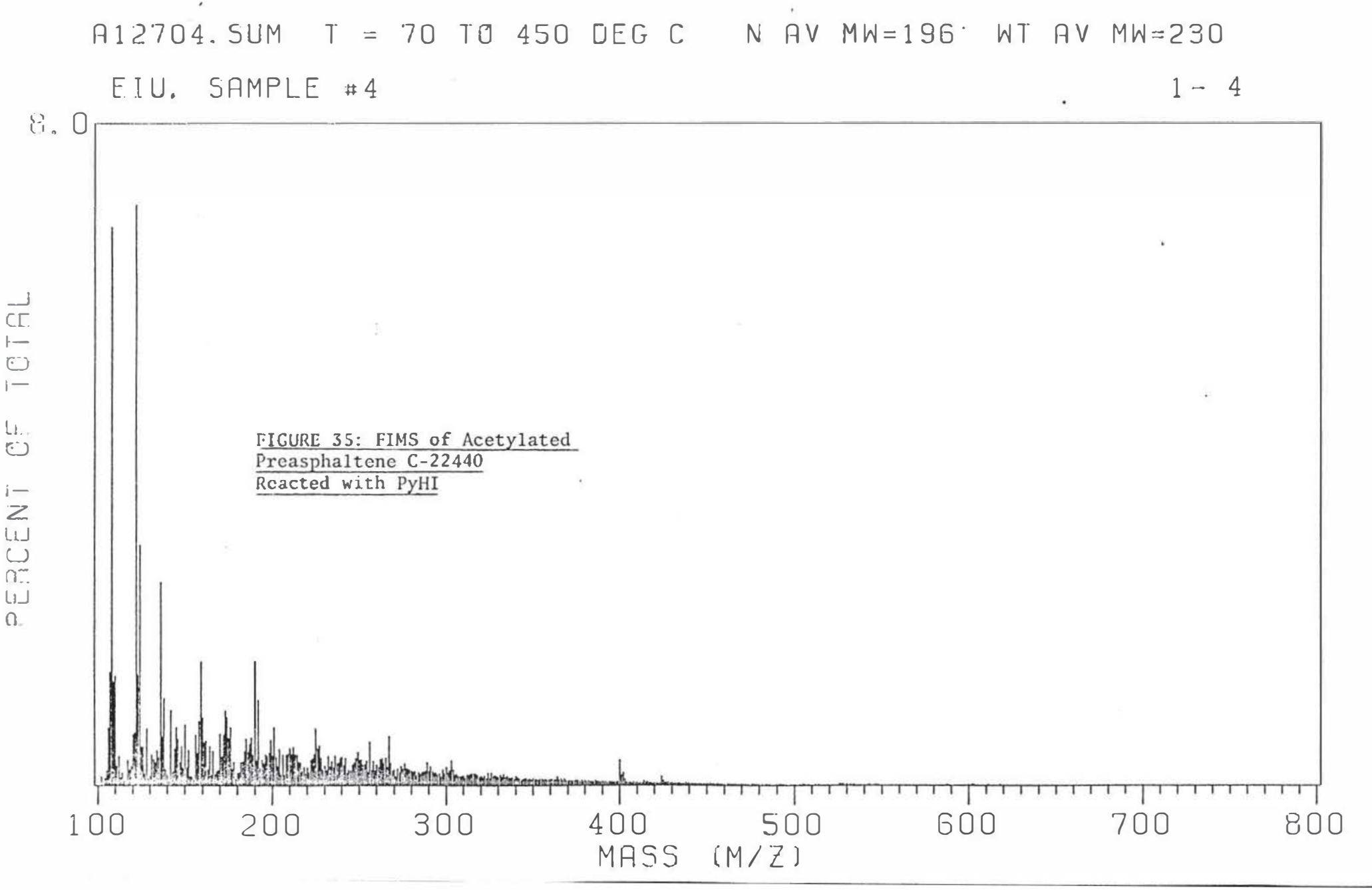


FIGURE 35: FIMS of Acetylated Preasphaltene C-22440 Reacted with PyHI

CONCLUSIONS

It appears that reaction of ferric chloride/acetic anhydride with coal fractions has little utility as an indicator of coal structure. The reaction conditions used give molecular condensation and no apparent ether cleavage in preasphaltenes. Reduction in reaction time and use of an aromatic solvent could result in an increase in solubility and a decrease in molecular weight.

Preasphaltenes are very susceptible to air oxidation. Researchers using the fraction must be aware of that fact. Phenol and molecular weight determinations should be done on preasphaltenes and products of preasphaltenes as soon as the product is isolated to avoid possible errors. Further work in this area is needed 1) to determine the actual chemical species generated in preasphaltenes by oxidation and 2) to account for the ease of oxidation of preasphaltenes with respect to coals as an indicator of structural differences.

Pyridine hydriodide in pyridine does not reduce the molecular weight of the two preasphaltenes studied. An increase in phenolic content occurs after reaction. The contrasting data of Mayo et. al. and this work give an opportunity to better understand the question of pyridine hydriodide cleavages in coal fractions. The following experiment is proposed as a method of final determination. Half of a sample of a pyridine hydriodide reacted preasphaltene should be washed in the manner of Mayo and

the other half washed as were the fractions in this work. Immediately after drying, molecular weights should be determined. Comparison of the results should give some insight into the matter.

Since coal work was done in several areas, no combined table of data is available in the main part of this thesis. Table 26, on the following page, contains all the data gathered on the coals, preasphaltenes and reacted preasphaltenes.

TABLE 26: Coal Data

	%C	%H	%N	%S	%O(diff)	%I	%Cl	%Ash	Phenol**	MW
252 Coal	69.36	4.52	1.54	1.84	7.12	----	0.13	15.62*	4.30	----
252 TIPS	72.77	5.22	2.78	----	18.01	----	----	1.23	4.28	----
282 Coal	73.19	4.98	2.09	0.71	7.26	----	0.22	11.78*	----	----
282 TIPS	76.38	5.37	2.49	1.03	13.43	----	----	1.25	4.78	1247
282 TIPS + $FeCl_3/C_4H_6O_3$	69.62	4.93	1.94	----	22.48	----	----	1.44	----	----
282 TIPS + PyHI	76.14	4.96	2.24	----	12.37	2.01	----	----	7.16	1119
Acet. 282 TIPS	72.99	4.83	2.36	0.54	18.03	----	----	----	----	----
Acet. 282 TIPS + PyHI	73.75	4.98	2.55	----	14.48	1.77	----	----	5.88	----
22440 Coal	68.76	4.92	1.10	4.16	11.26	----	----	9.80	----	----
22440 TIPS	78.23	5.50	2.23	1.08	12.08	----	----	0.88	4.44	1322
22440 TIPS + PyHI	72.54	5.26	2.03	----	12.15	6.06	----	----	7.06	1222
Acet. 22440 TIPS + PyHI	-----	----	----	----	----	----	----	----	5.31	----

*Percent mineral matter

**mmol g^{-1}

REFERENCES

1. Williams, J.M.Jr., Vanderborgh, N.E. and Walker, R.D., Los Alamos National Laboratory, University of California, Los Alamos, New Mexico 87545, draft prepared for the U.S. Department of Energy, Morgantown Energy Technology Center,, "Structural Concepts of Coal and Implications of Dynamic Interactions," p. 6.

2. Einstein, A, "Relativity", Crown Publishers Inc., New York, 1916, preface.

3. Haggin, J., Chem. and Eng. News, Aug. 9, 1982, No. 32 (17).

4. Owen, J., Fuel, 1981, 60 (755-61).

5. Stranges, A.N., J. Chem. Ed., 1983, 60 (617-25).

6. Kolb, K.E. and Kolb, D., J. Chem. Ed., 1983, 60 (57-9).

7. Shadle,L.J. and Given,P.H., Fuel, 1982,61 (972-9).

8. Gorbarty,M.L. and Ouchi,K., Eds., "Coal Structure", American Chemical Society, Washington D.C., 1981, preface.

9. Larsen, J.W., Ed., "Organic Chemistry of Coal", American Chemical Society, Washington,D.C., 1978 (50).

10. Durie, R.A., Fuel, 1982, 61 (884).

11. Halleux, A., Delevarenne, S. and Tchamler, H., Fuel, 1959, 38 (283-290).

12. Blom, L., Edelhausen, L. and van Krevelen, D.W., Fuel, 1957,36 (143).

13. DeWalt, C.W. and Glenn, R.A., Anal. Chem., 1952, 24 (1789-95).

14. Friedman, S., Kaufman, M.L., Stiener, W.A. and Wender, I.,Fuel, 1961, 40 (33-46).

15. Hofle, G. and Steglich, W., Synthesis, 1972 (619).

16. Larsen, J.W. and Kummerle, E.W., Fuel, 1976, 55 (162).

17. Mayo, F.R., Buchanan, D.H., and Pavelka, L.A., Fuel Division, Am. Chem. Soc., Preprints, 1980, 25, No. 2 (182).

18. Lazarov, L. and Angelova,G., Fuel, 1968, 47 (333).

19. Bhaumik,J.N., Mukherjee,A.K., Mukherjee,P.N. and Lahiri,A.,Fuel, London, 1962, 41 (443).

20. Jung,M.E. and Lyster,M.A., J. Org. Syn., 1977, 42 (3761).

21. Ganem, B. and Small, V.R.Jr., J. Org. Chem., 1974, 39, No. 25 (3728-9).

22. Davidson,R.M., "Coal Science", Academic Press, New York, Gorbarty,M.L., Larsen,J.W., Wender,I. Ed's, 1982 (102).

23. Larsen, J.W., Nadar, P.A., Mohammadi, M. and Montano, P.A., Fuel, 1982, 61 (889-93).

24. Davidson, R.M. , "Coal Science", Academic Press, New York, Gorbarty,M.L., Larsen,J.W., Wender,I. Ed's, 1982 (149).

25. Buchanan,D.H., Chen,A.M. and Sy,J.N.O., ACS Fuel Div. Preprints, 1984, 29(1) (220).

26. Fieser,L.F. and Fieser,M., "Reagents for Organic Synthesis", Vol. 1, John Wiley and Sons Inc., New York, 1967 (958-9).

27. Ibid. (274-5).

28. The ether was prepared by D. Luu, MS thesis, Eastern Illinois University, 1982.

29. Yoe,J.H., J. Am. Chem. Soc., 1932, 54 (4139).

30. Shatkay,A., Flavian,S., Analytical Chemistry, 1977, 49(14) (2222-7).

31. Chromatopac C-RIB Data Processor Instruction Manual, Shimadzu Corporation, Kyoto, Japan, 1982 (62-4).

32. Brandstorm,A., Berntsson,P., Carlsson,S., Djurhuus,A., Gustavii,K., Junggren,U., Lamm,B., and Samuelsson,B., Acta Chem. Scand., 1969, 23(2202-3).

33. Dockx,J., Synthesis, 1973 (441-56).

34. Dehmlow,E.V., Agnew. Chem. Internat. Edit., 1974, 13 (170-9).

35. Freedman,H.H. and Dubois,R.A., Tetrahedron Lett., 1975, 38 (3251-4).

36. Landini,D., Angela,M.M. and Montanari,F., J. Chem. Soc., 1975 (950-1).

37. Sjoberg,K., Aldrichimica Acta, 1980, 13 (55-8).

38. Starks,C., Chemtech, 1980 (110-17).

39. DePuy,C.H. and Fromsdorf,D.H., J. Am. Chem. Soc., 1957, 79 (3710-11).

40. Veeravagu,P., Arnold,R.T. and Eigenmann,E.W., J. Am. Chem. Soc., 1964, 86 (3072-5).

41. Mamedov,S.H. and Khydyrov,D.N., Zh. Obshch. Khim., 1962, 32 (1427-32).

42. Liotta,R., Fuel, 1979, 58 (728).

43. Saunders,W.H. and Edison,D.H., J. Am. Chem. Soc., 1960, 82 (138-42).

44. Papa,D., Schwenk,E. and Klingsberg,A., J. Am. Chem. Soc., 1946, 68 (2133-4).

45. Hodek,W. and Kolling,G., Fuel, 1973, 52 (220-5).

46. Olah,G.A., "Friedel-Crafts and Related Reactions," Vol. 4, Wiley, New York, pp 111-123.

47. Kovacic,P. and Volz,H.C., J. Am. Chem. Soc., 1959, 81 (3261-7).

48. Kovacic,P., Wu,C. and Stewart,R.W., J. Am. Chem. Soc., 1960, 82 (1917-22).

49. Kovacic,P. and Kyriakis,A., J. Am. Chem. Soc., 1963, 85 (454-8).

50. Kovacic,P. and Koch,F.W., J. Org. Chem., 1963, 28 (1864-7).

51. Mobley,D.P. and Bell,A.T., Fuel, 1979, 58 (661-6).

52. Fieser,L.F., and Fieser,M., "Advanced Organic Chemistry", Reinhold Publishing, London, 1965 (766).

53. Analysis was done by Reid Willis, University of Chicago.

54. Abdel Baset,Z., Given,P.H. and Yarzab,R.F., Fuel, 1978, 57 (95-9).

55. Messenger,L. and Attar,A., Fuel, 1979, 58 (656).

56. Gorbaty,M.L. and Ouchi,K., Eds., "Coal Structure", American Chemical Society, Washington, D.C., 1981 (289).

57. Hassner,A., Krepski,L. and Alexanian,V., Tetrahedron, 1978, 34(14) (2069-76).

58. Ignasiak,B.S., Clugstone,D.M. and Montgomery,D.S., Fuel, 1972, 51, (76-80).

59. Ignasiak,B.S., Szladow,A.J. and Montgomery,D.S., Fuel, 1974, 53 (12-15).

60. Wachowska,H.M., Nandi,B.N. and Montgomery,D.S., Fuel, 1974, 53 (212-19).

61. Painter,P.C., Snyder,R.W., Pearson,D.E. and Kwong,J., Fuel, 1980, 59 (282-6).

62. Morterra,C. and Low,M.J.D., Spectroscopy Letters, 1982, 15(9) (689-97).

63. Liotta,R., Brons,G. and Isaacs,J., Proc. Int. Kohlen-wisstag., 1981 (157-62).

64. It is not known if the Penn State analysis included grinding before analysis.

65. Mayo,F.R., Buchanan, D.H., Pavelka, L.A. and Hirschen, A.S., manuscript submitted to Fuel.

66. Master's Thesis, Eastern Illinois University, James Sy, 1983.

67. Gethner,J.S., Fuel, 1982, 61 (1273).

68. Billingham,N.C., "Molar Mass Measurements in Polymer Science," John Wiley and Sons, New York, 1977 (85-90).

69. Willard,H.H., Merritt,L.L., Dean,J.A. and Settle,F.A. Jr., "Instumental Methods of Analysis", D. Van Nostrand Co., New York, 1981 (567-72).

70. The spectra were recorded by Ripadaman Malhotra, Mass Spectrometry Program, Chemical Physics Laboratory, Stanford Research International.